A STUDY

OF THE

MECHANISM OF FILTRATION

P.C.CARMAN.

- INDEX -

Errata.

All values in dm.-kg.-sec units of "r" are 10^{-4} too low

The following is a list of the chief symbols used in the text, arranged in logical order:

V = Total volume of filtrate.

V_1 = Volume of filtrate up to the commencement of time readings.

V' = Volume of filtrate after the commencement of time readings,
i.e., $V = V' + V_1$

θ = Time taken to collect volume of filtrate, V'.
When $V_1 = 0$, as is usually the case in the literature, θ is the time taken to collect volume, V.

$dV/d\theta$ = Rate of filtration.

A = Area of filtering surface.

$1/A \cdot dV/d\theta$ = Rate of filtration per unit area of filtering surface, and thus measures the linear rate of filtration

P = Pressure of filtration, i.e., pressure difference across cake and cloth.

P_t = Absolute pressure of filtration, i.e., absolute pressure in the suspension on the cake side of the cloth.

P_b = Absolute pressure on the filtrate side of the cloth, or "back pressure",
i.e., $P_t = P + P_b$

P_0 = Pressure difference across cloth at the beginning of a constant rate experiment, i.e., initial value both of P and of P_1.

P_1 = Pressure difference across the cloth.

P_2 = Pressure difference across the cake,
i.e., $P = P_1 + P_2$

p = Frictional pressure loss of the liquid at a point in the cake, and the measure of unbalanced or deforming stresses upon particles in the cake.

t = Thickness of the cake.

v = Volume of cake deposited per unit volume of filtrate

i.e., vV = volume of cake $= tA$ or $t = vV/A$

c = Weight of cake solids deposited by unit volume of filtrate, measured by evaporating a known volume of slurry to dryness, and igniting. Both c and v measure concentration of slurry.

w = Weight of cake solids per unit area of filtering surface, and hence a measure of cake thickness,
i.e., cV = total weight of solids in the cake, $= wA$ i.e., $w = cV/A$

ρ = Resistance of the cake, defined from $dV/d\theta = P_1/\rho$

ρ_0 = Resistance per unit thickness of cake, i.e., $\rho = \rho_0 t$

ρ_1 = Resistance per unit volume of cake, i.e., $\rho = \rho_1 vV$.

ρ_1' = Constant in $\rho_1 = \rho_1' P^s$

s = Constant in $\rho_1 = \rho_1' P^s$, and, in general, in (resistance $\propto P^s$)

r_0 = Specific resistance of cake, i.e., resistance per unit cube, i.e., $\rho = r_0 t/A = r_0 vV/A^2$

r_0' = Constant in $r_0 = r_0' P^s$

r_0'' = Constant in $r_0 vV = r_0' P^s vV = r_0'' P^s \int_0^{vV} (1/A \cdot dV/d\theta)^k \cdot d(vV)$.

k = "Scouring effect" or "velocity effect" coefficient in $r_0 vV = r_0'' P^s \int_0^{vV} (1/A \cdot dV/d\theta)^k \cdot d(vV)$.

r_1 = "Specific resistance" as resistance per unit weight of cake per unit area, i.e., $\rho = r_1 w/A = r_1 cV/A^2$ and $r_1 w = r_0 t$

r_1' = Constant in $r_1 = r_1' P^s$

r'' & α = Constants in $r_1 = r''(1 + \alpha P)$.

r = "Specific resistance" as resistance per unit weight of cake per unit area at any point in the cake, $1/r_1$ is the average of $1/r$, i.e., $1/r_1 = 1/P \int_0^P dP/r$

r' = Constant in $r = r' p^s$, and $r_1' = (1-s) r'$.

ρ_c = Resistance of the cloth, defined by $dV/d\theta = P_1/\rho_c$

ρ_c' = Constant in $dV/d\theta = P^m/\rho_c'$ for the passage of clean water through a clean cloth.

m = Parameter in $dV/d\theta = P^m/\rho_c'$

n = $(m - 1)$, and is a constant in $\rho_c = \rho_c'/P^n$

i.e., $dV/d\theta = P_1/\rho_c = P_1 . P^n/\rho_c'$ and, for a clean cloth, where $P_1 = P$, $dV/d\theta = P^{n+1}/\rho_c' = P^m/\rho_c'$

R_1 = Cloth resistance per unit area, i.e., $\rho_c = R_1/A$

R_1' = Constant in $R_1 = R_1'/P^n$

w_0 = Weight of cake per unit area giving a resistance equivalent to the cloth resistance.

V_0 = Volume of filtrate which would be required to give w_0 i.e., $w_0 = cV_0/A$

η = Viscosity of filtrate.

a and b = Constants in $\theta/V' = bV' + a$

defined by $b = \eta r_1 c/2PA^2$

K = Constant in $a = 2b(V_1 + V_0)$

and in $dV/d\theta = K . P^{\cdot 27}/V^{\cdot 81}$

$dV/d\theta = K . P^{1-s/1+k}/V^{1/1+k}$.

A STUDY OF THE MECHANISM OF FILTRATION

Introduction.

The original intention of the present work was to investigate the filtering properties of suspensions of very finely-divided and of soft particles, which give cakes of slimy character. The majority of suspensions filtered in chemical industry belong to this general type, and, in dealing with them, pressure filters, such as the filter press and the leaf filter, are still used.

The chief factors which give rise to highly-resistant cakes are; (i) Smallness of particle size. In a cake composed of small particles, the voids between the particles are very small. Since, according to Poiseuille's Law, the rate of flow in a circular capillary varies in direct proportion to the fourth power of the diameter of the tube, the rate of flow through a cake composed of small particles will be very slow.

(ii) Softness of particles. A particle of gelatinous nature, such as a floc of ferric hydroxide, will tend to deform inside the cake in such a manner as partially to block up the voids in the cake.

It was at first decided to study the first of these effects, i.e., particle size. A review of the literature, however, revealed that there was no satisfactory technique

for measuring cake resistance. The usual method for comparing rates of flow has been to measure the time taken to filter a standard volume of slurry under standard conditions of slurry concentration, area of filtering surface, and viscosity of filtrate. It was not felt that such a method could produce results of general value.

This thesis is, therefore, mainly a study of the mechanism of filtration with the intention of establishing general laws, and thence a technique for research. Towards the end of the thesis is an account of the application of this technique to the use of filter aids, and to the interpretation of their action.

The general filtration equation which is derived has been applied by the writer to the economics of filtering, e.g., for calculating the most economical size of filter, the optimum length of cycle, the most efficient proportion of filter aid, etc.; but this has not been included in the thesis.

I. T H E O R E T I C A L.

Resume of the literature.

The first theoretical study of filtration was that of Hatschek[1] in 1908. He obtained experimental evidence to prove that the layer of particles first deposited upon a filtering medium gave an abnormally high resistance; and he pointed out the importance of microscopical study of the type of particles in a slurry, in research upon filtration problems.

Microscopical study is not, however, sufficient, for it is essential, first of all, to be able to interpret quantitative measurements upon the rate of filtration, in order to correlate such measurements with microscopical observations of the type of particles being filtered. Even at the present day, however, the interpretation of data on rate of flow is a field for conflicting theories.

Almy and Lewis[2], in 1912, were the first to enter this field of work. From six constant pressure filtrations, using six different pressures of filtration, they derived the empirical equation (1), in which P is the pressure of filtration and V is the volume of filtrate in time, θ, K being a constant.

$$dV/d\theta = K \cdot P^{.27}/V^{.81} \quad . \qquad (1$$

In addition, they performed two experiments to find

the effect of viscosity. They formed a cake at 25 lbs./sq.in., and passed through this in turn, clean filtrate, which contained a considerable percentage of dissolved salts, filtrate diluted with an equal quantity of water, and pure water, keeping the pressure at 25 lbs./sq.in. The rates of flow were almost exactly in inverse proportion to the viscosities of these liquids, 1.24 : 1.09 : .96 centipoises.

Further, they found that, for such a cake, the rate of flow is proportional to the pressure, provided that the pressure does not exceed that at which the cake was deposited. The compressibility of such a cake is not, therefore, reversible.

In 1916, Sperry[3] derived a theoretical equation, by applying Poiseuille's Law. For a circular capillary, this Law is $dV/d\theta = \pi P D^4/128\eta L = P/K_1 L$

where D = diameter and L = the length of the capillary, η = the viscosity of the liquid, P = pressure difference between the ends of the capillary, and K_1 = a constant when D and η are maintained constant. Sperry assumed any porous medium to be equivalent to a bundle of equally-sized, parallel, circular capillaries, so that the rate of flow through a filter cake is given by $dV/d\theta = P/\rho_0 t$. (2

where t = thickness of the cake, P = pressure of filtration, and ρ_0 = a constant for unit thickness of cake. He recognised also that the filter medium must be taken into account, so

that his equation becomes

$$dV/d\theta = P/\rho_0 t + \rho_c \quad . \quad . \quad (3$$

where ρ_c a constant for the filtering medium. The thickness of the medium need not be taken into account, since it is a constant.

The thickness of the cake is proportional to the volume of filtrate, V, multiplied by the concentration of the slurry, v, where v = volume of cake deposited by unit volume of filtrate, whence $\rho_0 t = \rho_1 v V$

$$\text{i.e., } dV/d\theta = P/\rho_1 v V + \rho_c \quad . \quad . \quad (4$$

Sperry tested his equation (4) with a number of materials varying from kieselguhr to starch, and found quite good agreement. For substances like starch, however, ρ_1 varied when the pressure of filtration was varied, so that it was necessary to write $\rho_1 = \rho_1' P^s$

$$\text{i.e., } dV/d\theta = P/\rho_1' P^s v V + \rho_c \quad . \quad (5$$

Later, Hinchley, Ure and Clarke[4] tested equation (4) further, using magnesium and calcium carbonates and barium phosphate, all carefully precipitated to give coarse particles and hence ideal cakes. They found the Sperry equation represented their results within the accuracy of the experiments, each material giving a value of ρ_1, independent of pressure, P, or of concentration, v.

Sperry did not include a term for area in equation (4), so that ρ_1 would give a different value for

each change of area. This was recognised later by Lewis[5] and his co-workers, who introduced the useful analogy between the equation for rate of filtration and Ohm's Law in electricity.

Ohm's Law is $I = E/R$

i.e., current = potential difference / resistance;

and the filtration equation, based on analogy to Poiseuille's Law, is $dV/d\theta = P/\rho = P/\rho_0 t$

where $\rho = \rho_0 t$

i.e., rate of flow = pressure of filtration / resistance

Then, just as electrical resistance = $\frac{\text{specific resistance} \times l}{\text{cross-sectional area}}$

where l = the length of the conductor,

so filtration resistance = $\frac{\text{specific resistance} \times \text{thickness}}{\text{area of filtering surface}}$,

i.e., $\rho = r_0 t/A$

where r_0 = specific resistance = resistance of unit cube,

A = area of filtering surface.

Further, thickness = $\frac{\text{total volume of cake}}{\text{area of filtering surface}}$,

i.e., $t = vV/A$

i.e., $\rho = r_0 v V/A^2$

whence $dV/d\theta = PA^2/r_0 v V$

If cloth resistance be introduced, we have

$$\rho_c = R_1/A$$

where R_1 = resistance per unit area of the cloth, so that

$$dV/d\theta = PA^2/r_0 v V + AR_1 \quad . \quad . \quad (6$$

Equation (6) is the form applicable to ideal cakes. It can be modified for compressible cakes by putting $r_0 = r_0' P^s$

i.e., if cloth resistance be neglected, we get

$$dV/d\theta = P^{1-s} \cdot A^2/r_o' v V \quad . \quad . \quad (7$$

Equation (7) is that recommended by the Lewis school for "homogeneous cakes", i.e., cakes in which the particles have all approximately the same size. For "heterogeneous cakes", in which fine particles are mixed with relatively coarse ones, a "scouring effect" is assumed. According to this, the specific resistance, r_o , depends upon the linear rate of flow through the cake, which is itself proportional to the value of the volume rate of flow per unit area, i.e., to $1/A \cdot dV/d\theta$. Then, as the effect must be cumulative, we obtain

$$r_o v V = r_o' \cdot P^s \cdot v V = r_o'' \cdot P^s \int_o^{vV} (1/A \cdot dV/d\theta)^h \cdot d(vV)$$

$$= r_o'' \cdot P^s v / A^h \cdot \int_o^V (dV/d\theta)^h \cdot dV$$

i.e., $$dV/d\theta = P^{1-s} \cdot A^{2+h} / r_o'' \cdot v \int_o^V (dV/d\theta)^h \cdot dV \quad . \quad (8$$

In 1926, Underwood[6] advanced a new rate equation, based upon part of the work of Hinchley, Ure and Clarke.[4] These workers found that, for clean cloths, and for cloths with only a small thickness of cake upon them, rate of flow was not directly proportional to pressure, as required by Sperry's assumption. In Fig.1., curves A, B, and C, respectively, represent a heavy, chain-weave cloth, a fine, twill-weave cloth, and a monel metal cloth. None of these curves is a straight line passing through the origin, as would be the case if rate of flow were directly proportional to pressure. Underwood pointed out that curves A and C, respectively, could be represented by the equations $dV/d\theta = P^2/.027$ and $dV/d\theta = \sqrt{P}/.00028$.

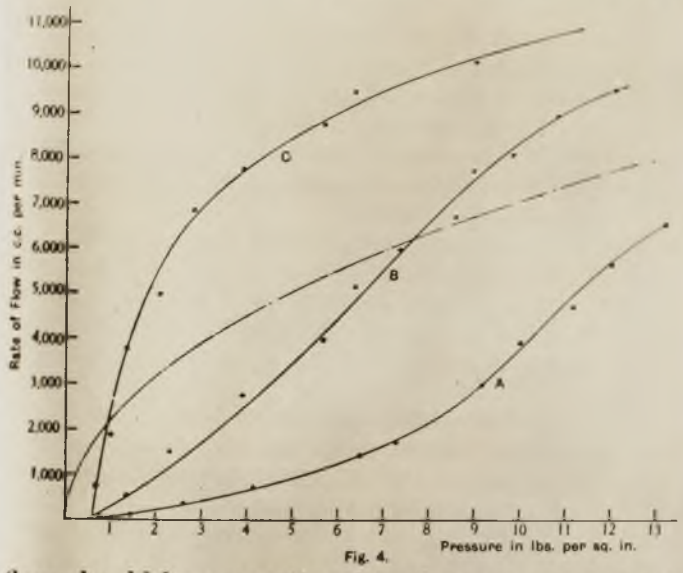


Fig. 4.

flow should be proportional to the square root of the pressure, and that at this point the resistance of the cloth reaches a maximum.

900

Fig.1.

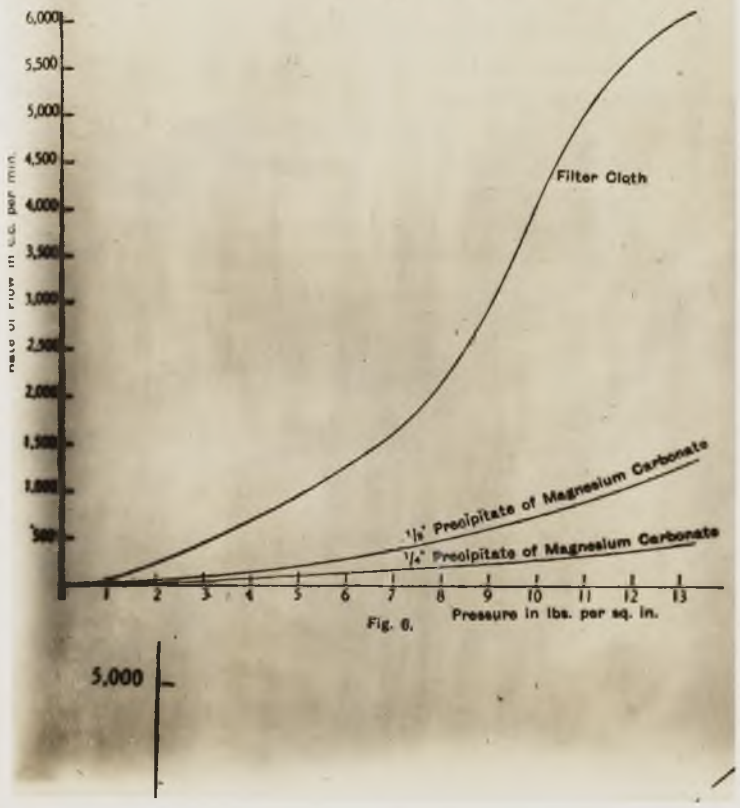


Fig. 6.

5,000

Fig.2.

He assumed, therefore, that the general equation for rate of flow through a clean cloth was

$$dV/d\theta = P^m/\rho_c' \qquad (9$$

where ρ_c' = constant, and m can have values between 2 and $\frac{1}{2}$, according to the type of cloth. When there is a cake upon the cloth, the filtration pressure is divided into a drop of pressure across the cloth, P_1 , and a drop of pressure across the cake, P_2 , where $P_1+P_2 = P$. By assuming that a cake on the cloth makes no difference to the behaviour of the cloth, Underwood gave equation (9) the more general form,

$$dV/d\theta = P_1^m/\rho_c' \qquad (10$$

When $m=1$, the cloth obeys Poiseuille's law, and we get the Sperry equation, $dV/d\theta = P_2/\rho_1 vV = P_1/\rho_c = P/\rho_1 vV+\rho_c$

But, when $m \neq 1$, we get the Underwood equation as a more general form, as follows:

$$P_1 = (\rho_c' \cdot dV/d\theta)^{1/m}$$

$$P_2 = \rho_1 v V \cdot dV/d\theta$$

$$P = P_1 + P_2$$

$$= (\rho_c' \cdot dV/d\theta)^{1/m} + \rho_1 v V \cdot dV/d\theta. \qquad (11$$

This equation was tested with Hinchley, Ure and Clarke's results for rate of flow through thin cakes, and appeared to give a satisfactory interpretation of these results.

In a later paper, Underwood[7] put forward a theory for compressible cakes. As this will be discussed later, and criticised, it will not be dealt with at this point.

In order to present the work of Gilse, Ginneken and Waterman,[8] it is advisable to convert equation (2) to a form slightly different from that in equation (4). Cake thickness, t, is proportional to the weight of cake per unit area, w, so that it is possible to write $r_0 t = r_1 w$

i.e., cake resistance $\rho = r_0 t/A = r_1 w/A$

where r_1 is the resistance of unit weight of cake per unit area of filtering surface. It is thus analogous to a specific resistance, and, hence forward, the term, specific resistance, will apply to r_1, not to the specific resistance of a unit cube, r_0, which has so far been used.

The filtration equation becomes

$$dV/d\theta = PA/r_1 w + R_1 \quad . \quad . \quad (12$$

The advantage of using w instead of t is that it is much more easy to measure weight of cake per unit area than to measure cake thickness, for w is given by

$$w = cV/A \quad . \quad . \quad (13$$

where c = weight of cake material per unit volume of filtrate a quantity which is very easily obtained. It should be noted that by "weight" is meant the dry weight, since this eliminates any uncertainty in the determination of w or of c. Substituting the value of w in equation (12), we obtain

$$dV/d\theta = PA^2/r_1 cV + AR_1 \quad . \quad . \quad (14$$

Equation (12) was the form favoured by Gilse, Ginneken and Waterman, who deduced it from their experimental results. The results of these workers are the most reliable and most complete to date, for, instead of publishing

three or four experiments, they have published the full data for nearly ~~fifty~~ thirty filtrations. Furthermore, they recognised the importance of viscosity, and carried out all experiments at a constant temperature of 20°C. Actually, the equation finally presented by Gilse, Ginneken and Waterman was

$$dV/d\theta = PA/r''(1+\alpha P).w$$

i.e., the cloth resistance, R_1, was found to be negligible in their experiments, and the specific resistance, r_1, varied with the pressure of filtration, P, according to $r_1 = r''(1+\alpha P)$. This is mainly of importance in that the results of Lewis and of Sperry lead to a different result, $r_1 = r_1' P^s$.

Gilse, Ginneken and Waterman also carried out an experiment involving a change of area. They determined the constants, r'', and α, upon a small filter, of .4534 sq.dm. area of filtering surface. Then, using the same material, they used a laboratory filter press of 13.4 sq.dm. of filtering surface. For a given value of P and a given value of w, the values of $dV/d\theta$ were found to be within 5% of the expected ratio, .4534 : 13.4, for the two filters, which was within the limits of experimental error.

To summarise briefly, most published experiments are in agreement with equation (14),

$$dV/d\theta = PA^2/r_1 cV + AR_1$$

when we take r_1 as a constant for ideal cakes and as a function of P for compressible cakes, e.g., $r_1 = r_1' P^s$ and $r_1 = r''(1+\alpha P)$. It does not agree with the empirical equation (1

$dV/d\theta = K.P^{.27}/V^{.61}$, of Almy and Lewis. Underwood[6] has shown, however, that the data upon which they based their equation are much better represented by

$$\theta/V = bV + a$$

where b is proportional to $1/P^{.26}$. Differentiated, this gives

$$dV/d\theta = 1/2bV + a$$

which is of the same form as equation (14).

Opposed to equation (14), we have equation (8), based on the Lewis "scouring effect", and the Underwood equation (11), based on Underwood's theory of cloth resistance. The following section will be devoted to a criticism of these two equations.

Criticism of Lewis and of Underwood Equations.

The Lewis equation for "scouring effect",

$$dV/d\theta = P^{1-s} A^{2+k}/r_o'' v \int_o^V (dV/d\theta)^k dV$$

is advocated for "heterogeneous" slurries, i.e., slurries in which we have a mixture of large and of small particles. The velocity term, $(dV/d\theta)^k$, is introduced to allow for the tendency of the liquid, on its way through the cake, to sweep small particles from the position in which they first lodged to a position deeper in the cake, so that the deepest parts of the cake become plugged with small particles and highly resistant. Underwood has criticised the physical reality of this scouring effect, and considers the term, $(dV/d\theta)^k$, is purely empirical. Ruth, Montillon and Montonna[9] have pointed out that equation (8) transforms to an equation similar to the

empirical equation (1) of Almy and Lewis, and that it is difficult to explain why a homogeneous slurry such as chromium hydroxide, to which equation (1) applies, should exhibit a "scouring effect".

The equation can, however, be given a different physical basis, applicable to all compressible cakes, as has been suggested by Donald.[10] This is based upon the observation that a compressible cake contains a higher percentage of water and hence a higher percentage of voids at the surface than at the cloth. We can suppose that a soft particle, suddenly stopped at the surface of the cake, is deformed by the impact. The more it is deformed, the greater will be the specific resistance at that point, as the particles will be more tightly packed together. As the impact depends upon the linear velocity of approach, and hence upon $1/A \cdot dV/d\theta$, the percentage of voids of successive layers will increase, and the corresponding specific resistance decrease, owing to the diminishing value of $dV/d\theta$. If the specific resistance of a layer is proportional to $\left(1/A \cdot dV/d\theta\right)^h$, where $dV/d\theta$ was the rate of flow when this layer was deposited, then, if also the layer be of infinitesimal thickness, dt, its resistance, $d\rho$, is given by

$$d\rho = r_0 \cdot dt/A = r_0 d(V)/A^2 = r_0' P^s v \cdot dV/A^2$$
$$= r_0'' P^s \left(1/A \cdot dV/d\theta\right)^h v \, dV/A^2$$

$$\text{i.e.,} \quad \rho = r_0'' P^s V/A^{2+h} \cdot \int_0^V (dV/d\theta)^h dV$$

$$\text{i.e.,} \quad dV/d\theta = P/\rho = P^{1-s} A^{2+h} / r_0'' v \int_0^V (dV/d\theta)^h dV$$

which is the same as equation (8). Thus equation (8) can be given quite a good physical foundation, and to distinguish the underlying theory, it is proposed to replace the term, scouring effect, by "velocity effect".

Equation (8) transforms to

$$dV/d\theta = \left\{ A^{2+k}/\tau_0'' v (1+k) \right\}^{1/1+k} \cdot P^{1-s/1+k} / V^{1/1+k}$$

Then, if area, A, and concentration, v, be constant,

$$dV/d\theta = K . P^{1-s/1+k} / V^{1/1+k}$$

which is of the same form as equation (1); but, as we have seen already, equation (1) has not any experimental foundation, for the data published by Lewis and Almy in its support agree more closely with a specialised form of equation (14).

Upon integrating at constant pressure, we obtain

$$V^{2+k/1+k} = K'\theta$$

where K' is a constant, so that the plot of log.V vs. log.θ should give a straight line of gradient $^{1+k}/_{2+k}$. Donald and Hunneman[11] have carried out a single experiment which appears to confirm this, the points for log.V vs. log.θ lying on a straight line of gradient,.91.

Equation (14), integrated under the same conditions, gives

$$V^2 + K''V = K'''\theta$$

where K'' and K''' are constants. If, as is assumed in the derivation of equation (8), cloth resistance be considered negligible, this becomes

$$V^2 = K'''\theta$$

whence the gradient of log.V vs. log.θ is .5, which is, of course, given by $^{1+k}/_{2+k}$ only when $k = 0$, i.e., when there

is no velocity effect. If, however, cloth resistance is not negligible, the gradient of log. V vs. log. θ is at all times greater than .5, and, further, as a log.-log. plot expands the scale for low values of V, and contracts it for large values, those values of V which are most prominent in such a plot are just the values which are most influenced by neglect of cloth resistance. In short, experimental values, which obey equation (14), will tend on a log.-log. plot to scatter about a fairly straight line, the gradient of which is very considerably in excess of .5. The nature of Donald and Hunneman's experiment did, in fact, suggest that the cloth resistance was not negligible, so that their gradient of .91 is not very satisfactory evidence for equation (8).

Weber and Hershey[12] published four experiments of a like nature, but extrapolated the V vs. θ curves to $V=0$, cutting the θ-axis at θ_o. They then plotted log. V vs. log. $(\theta - \theta_o)$ and obtained gradients, .3, .42, .55, .54. By using this correction, then, the gradients have been brought much nearer to .5. This is what we should expect from equation (14), however, and, indeed, if we write the integrated form as

$$V^2 = K'''\theta - K''V$$

i.e.,

$$V^2 = K'''\{\theta - K''V/K'''\}$$

it will be seen that cloth resistance cannot be allowed for by a term, θ_o, where θ_o is a constant, so that such a correction would not be likely to reduce the gradient exactly

to .5.

In short, while these data appear to favour equation (8) at first sight, they are easily explained away as deviating from equation (14), either because a very considerable cloth resistance has been neglected, or because the wrong type of correction has been used for it.

To turn now to the Underwood equation (11), it has already been noted that this was based upon the data of Hinchley, Ure and Clarke for the flow of clean water through clean cloths, as given in Fig.1. Underwood showed that the curve for Cloth A was a parabola of the type, $dV/d\theta = P^2/\rho_c'$, and, Cloth C, a parabola of the type, $dV/d\theta = \sqrt{P}/\rho_c'$. He deduced, therefore, that the general equation for rate of flow through clean filter cloths was $dV/d\theta = P^m/\rho_c'$, where ρ_c' is a constant for any particular case and m can have values between the limits $m = 2$ and $m = \frac{1}{2}$. Cloth C, however, for which $m = \frac{1}{2}$ is a monel metal cloth, much more open in texture than the cotton cloths, and giving a much higher rate of flow, as shown by Fig.1. Now, Poiseuille's Law, for which $m = 1$, applies only to stream-line flow. For turbulent flow, we do, indeed, get $dV/d\theta = P^m/\rho_c'$, where $m < 1$, so that the curve for monel metal cloth seems to indicate turbulent flow. If we turn to Fig.2., which represents the effect of cakes of magnesium carbonate of varying thicknesses upon the rate of flow through Cloth A, it will be seen that the rates of flow are in no way comparable with the rates of flow

through a clean monel metal cloth. It appears justifiable, therefore to assume that turbulent flow has no importance in filtration problems, which are always concerned with the presence of a cake. Values of $m < 1$ have thus no interest for us.

Values of $m > 1$ are probably due to the non-rigid character of the cloth. A very simple explanation put forward by Underwood is that the cloth is supported only at parts of its surface, so that the pressure upon it causes it to bulge between these points of support. The consequent stretching of the fibres in the cloth will cause the pores to enlarge, with a corresponding decrease in the resistance of the cloth. If, then, ρ_c be the resistance of the cloth, ρ_c will be a function of P, the pressure of filtration, and can be represented by $\rho_c = \rho_c' / P^n$, where n is a constant and is positive. Then, if Poiseullle's Law can be assumed for the enlarged pores we have

rate of flow = pressure / resistance

i.e., $$dV/d\theta = P/\rho_c = P \cdot P^n/\rho_c' = P^m/\rho_c'$$

where $m = n+1$. If this be the true explanation for values of $m > 1$, it is impossible to assume that, when we have a cake upon the cloth $$dV/d\theta = P_1^m/\rho_c'$$

But we must write

$$dV/d\theta = P_1/\rho_c = P_1 \cdot P^n/\rho_c' \quad . \quad . \quad (15$$

for, as the cake no tensile strength, ρ_c will have the same value for a given value of P, whether cake be present or

not.

Equation (15) does not lead to Underwood's equation, but to a modified form of the Sperry equation

$$dV/d\theta = P/p_1 V + p_c'/P^n \quad . \quad . \quad (16$$

or, including terms for area, A, and replacing V by c,

$$dV/d\theta = PA^2/r_1 cV + AR_1'/P^n \quad . \quad . \quad (17$$

Since the physical explanation used by Underwood leads rather to equation (16) than to equation (11), and since the former is the simpler to use, equation (11) cannot be considered to have any validity unless very definite experimental evidence can be found for it. Underwood applied the data of Hinchley, Ure and Clarke to test his equation, and appeared to obtain concordant results. If, however, we use analogous methods of plotting, based upon equation (16), we find just as good an agreement, and, indeed, the results have not sufficient accuracy to justify any hypothesis.

There is, therefore, no justification for considering either the Lewis or the Underwood equation a more general form than equation (14).

Modification of Equation (14).

In the previous section, equation (14)

$$dV/d\theta = PA^2/r_1 cV + AR_1$$

was established as a general form applicable to all types of filtration, so far as can be judged from the small amount of reliable, published data. In this equation, r_1 is a

constant for ideal cakes, but depends upon the value of P for compressible cakes. If equation (17) be admitted as having a slightly greater generality than equation (14), we must consider that R_1 also depends upon P, according to $R_1 = R_1'/P^n$, where R_1 is the resistance per unit area of filter cloth. Another form of equation (14) is given by equation (12), $dV/d\theta = PA/r_1 W + R_1$

in which W = weight of cake per unit area = cV/A; and equation (12) may be written as

$$dV/d\theta = PA/r_1(W + W_o) \quad . \quad . \quad (18$$

where $W_o = R_1/r_1$ = constant at constant pressure, R_1 and r_1 being both dependent upon pressure alone. For an ideal cake and ideal filter medium, W_o is a constant, independent of pressure, and is to be compared with a similar constancy when both cake and cloth have equal compressibility, as is assumed later on in the derivation of equation (23).

A physical meaning can be given to W_o, for it is the weight of cake per unit area which would be required to give a resistance equal to that of the cloth. Then, just as $W = cV/A$, it is permissible to define a new quantity, V_o, such that $W_o = cV_o/A$,

i.e., $$dV/d\theta = PA^2/r_1 c(V + V_o) \quad . \quad . \quad (19$$

Now, according to Poiseuille's Law, rate of flow should be inversely proportional to viscosity, so that equation (14), and its derivatives, would be true only for a liquid of unit viscosity. Adding, therefore, a term for

viscosity, η , we obtain

$$dV/d\theta = PA/\eta(r_1 w + R_1)$$

$$= PA/\eta r_1 (w + w_0) \quad . \quad . \quad (20$$

$$= PA^2/\eta r_1 c (V + V_0) \quad . \quad . \quad (21$$

Defects in the Theory for Compressible Cakes.

Equation (14), when applied to ideal cakes, derives from Poiseuille's Law. For compressible cakes, it has been usual to assume that the specific resistance, r_1 , is a function of the pressure of filtration, P , and hence that, just as for ideal cakes, it is the same at all points of the cake for any given pressure of filtration.

Underwood has suggested a physical basis for this assumption. When a layer of particles strikes a cake, it is subjected to the total pressure of filtration, P , so that, as each layer in the same way is subjected to the same pressure, P , the specific resistance is the same at all points of the cake, and its value is determined by the value of P . Thus we may write $r_1 = r_1' \cdot P^s$, and equation (14) follows at once.

Cake compressibility can result from a decrease in particle size, or from a change in particle shape, as particles become squeezed closer together, or from both effects. Decrease in particle size, without change of shape, results from a pressure applied with equal intensity at all points on

the surface of the particle, whereas deformation occurs when the particle is subjected to pressures of unequal intensity, e.g., to a low pressure in the voids between the particles and to a high pressure at the surfaces of contact with other particles. It will be shown shortly that, if deformation be assumed to take place, the specific resistance must vary from point to point in the cake.

Underwood's theory, therefore, really means that cake compressibility is due wholly to the compression of the particles, without appreciable deformation; for, as the particles are subjected to the full intensity of pressure in the liquid, before they ever reach the cake, they are not likely, in the cake, to become any smaller. Each layer, therefore, contributes the same increment of resistance and the specific resistance is the same at all points of the cake. The compression of the particle depends upon the absolute pressure within the filter, i.e., upon P_t , where $P_t = P + P_b$, P being the pressure of filtration and P_b the absolute pressure on the filtrate side of the cloth. Then $r_1 = F(P_t)$ where $F(P_t)$ = a function of $P_t = F(P + P_b)$. If we make the somewhat unlikely assumption that the function, $F(P_t)$, can take the form $\phi(P_b) \cdot P^s$, where $\phi(P_b)$ is a function of P_b , we have an equation analogous to $r_1 = r_1' P^s$, in which $r_1' = \phi(P_b)$ and is a constant so long as the back pressure, P_b , is a constant. It is, therefore, implicit in Underwood's theory

that r_1' depends upon P_c, so that, if we alter P_c, e.g., by using vacuum filtration instead of positive pressure filtration, r_1' must change in value.

It will be shown in the experimental part of this thesis that r_1' does not alter in value when vacuum filtration is used, so that the above theory must be discarded.

The alternative explanation is that cake compressibility is due to particle deformation, and that the effect of pressure upon the size of the particle is negligible. This is, indeed, a reasonable assumption, if we consider that substances which give compressible cakes are flocculent in nature. The cake-building particle is the floc, which is soft and easily deformed by unbalanced pressures, but which shows hardly any change of size when an evenly-distributed pressure is applied, owing to the ease with which liquids can penetrate to all parts of its loose structure.

Evidence for particle deformation is provided by study of the distribution of water in a cake. Philipp,[13] Young,[14] and Ruth, Montillon and Montonna[9] have all pointed out that the composition of a cake is not constant at all points, as would be the case if the specific resistance were the same at all points of the cake. A cake of ferric hydroxide or of Prussian blue is hard and dry at the cloth and so wet at the surface that it is hardly distinguishable from the slurry. Actual measurements of the water-content at various sections

of the cake have confirmed these observations. Since the water-content measures the proportion of voids in a cake, a low water-content means a low proportion of voids and hence a high specific resistance, and vice versa. Evidently, the specific resistance of a compressible cake is not uniform at all points, being least at the surface and greatest at the cloth-face.

The reason for this is seen if we consider that a cake is compressed by deformation of the particles within it. A particle in the cake is in contact with other particles and with the liquid flowing past it. The particles in the cake form a skeleton which transmits the hydrostatic pressure, P, to the cloth and thence to the cloth supports; but the liquid, as it passes through the cake, progressively loses pressure, commensurate with the friction which has been overcome. Fig.3 shows a particle in the cake in contact with four other particles. Wherever there is contact between particles, the total pressure, P, is transmitted. But, in the liquid occupying the voids, the pressure has been reduced from P to $(P-p)$, where p is the pressure lost to friction in the passage of the liquid from the surface of the cake to the given point. The particle is thus subjected to an unbalanced or deforming pressure measured by $P-(P-p)$, i.e., p, and takes the shape shown in Fig.4. This deformation causes a reduction of the size of the pores, with a consequent increase

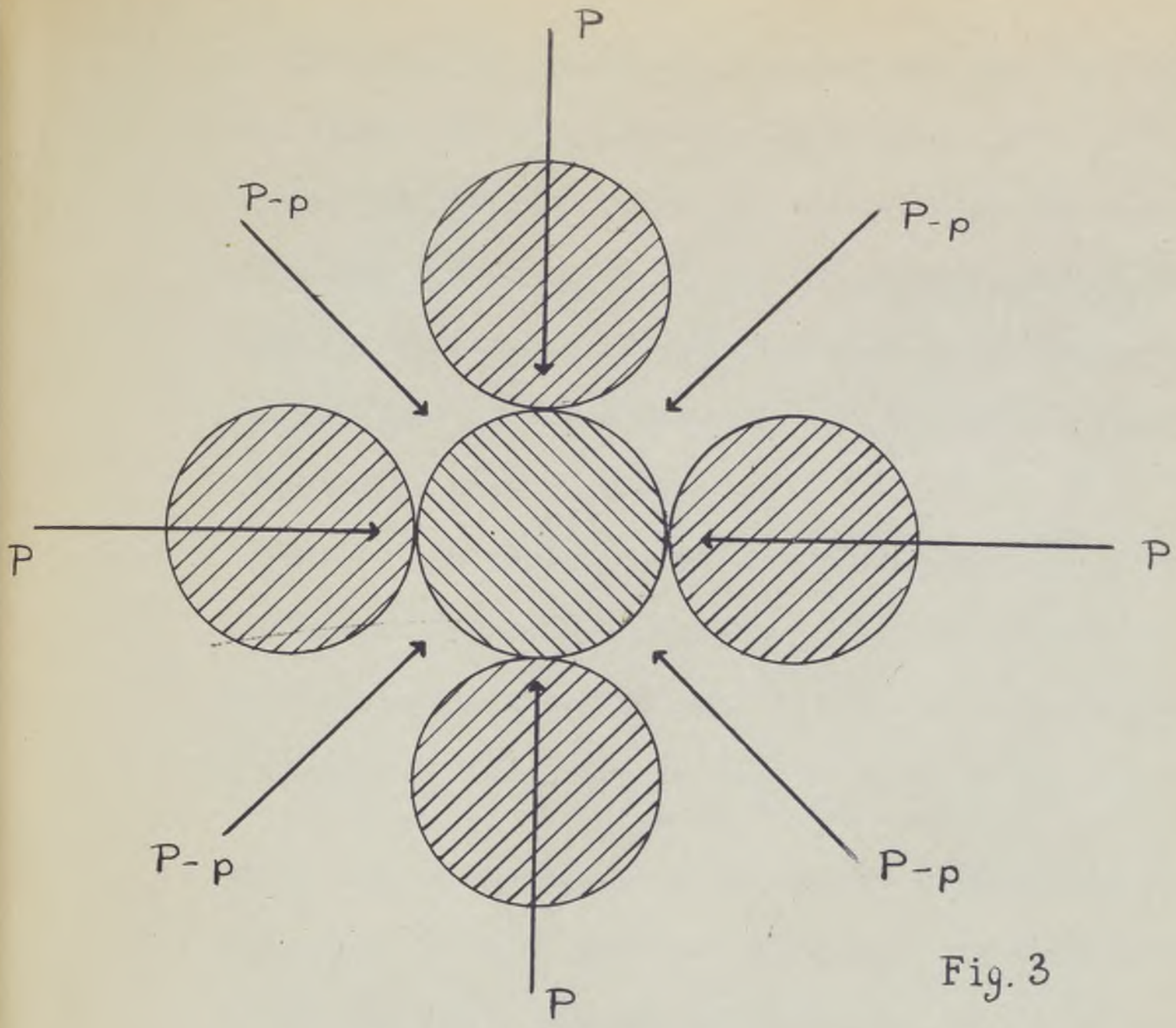


Fig. 3

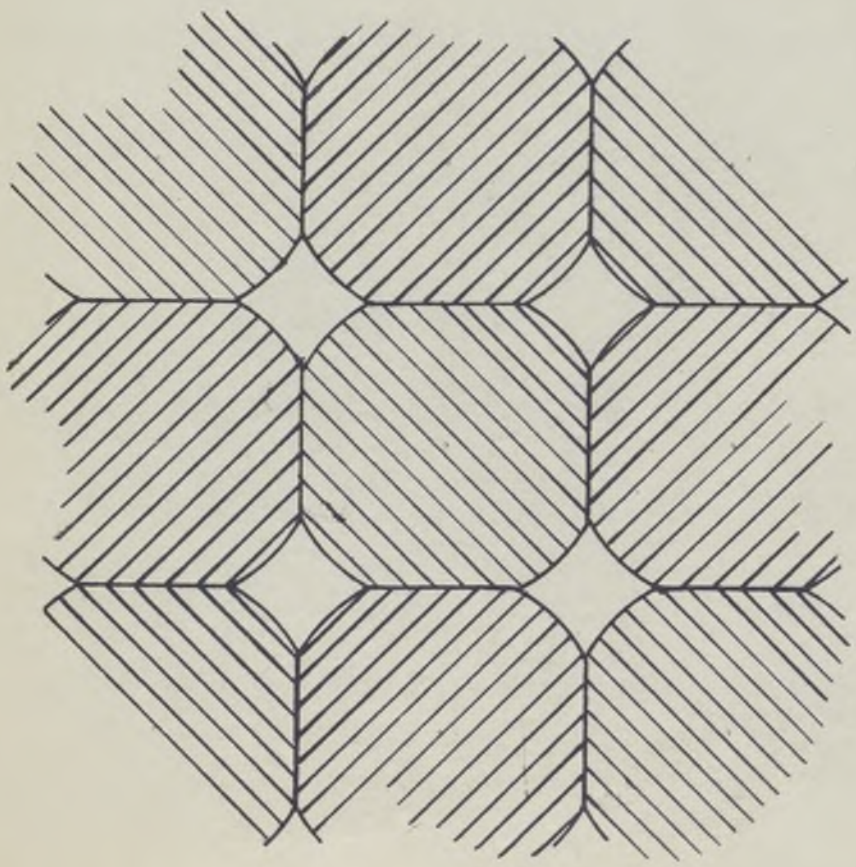


Fig. 4

of the specific resistance. It follows that the specific resistance at any point is some function of p, and of p alone. Furthermore, since p is zero at the surface of the cake, and increases to P_2 at the surface of the cloth, the specific resistance of the cake will be least at the surface and greatest at the cloth-face, in accordance with the experiments upon water-content.

If the deformation of the particles increases continuously from cross-section to cross-section of the cake, Poiseuille's Law can be applied only over an infinitesimal thickness of the cake, so that we must write,

$$dV/d\theta = dp.A/\eta r.dw \quad . \quad . \quad (22)$$

where dp is the pressure difference across this infinitesimal thickness of cake, dw is its weight per unit area, and r is its specific resistance. According to the above theory, r is a function of p alone, so that it is possible to integrate equation (22)

$$dV/d\theta = PA/\eta r_1 (w+w_0) \quad . \quad . \quad (23)$$

where $$1/r_1 = 1/P \int_0^P dp/r$$

By assuming that, when $p = P$, $w = w + w_0$, we have assumed that the integration can be taken through both cake and cloth, i.e., that both cake and cloth have the same compressibility. This is, perhaps, rather too wide an assumption, and the general case, where cake and cloth have different degrees of compressibility, is given in Appendix I. This more general

treatment gives the same equation (23), as an approximation correct within the limits of experimental error, provided the cloth be well covered with a layer of cake. The main point of difference in the general case is that the quantity, w_o, is not a constant, independent of pressure, as it is in the above special case, when both cake and cloth have the same compressibility.

Equation (23) can be given in the form

$$dV/d\theta = PA^2/\eta r_1 c (V+V_o) \quad . \quad . \quad . \quad (24$$

The theoretical equation (23) is of the same form as the experimental one, equation (20), the specific resistance, r_1, being, in both cases, a function of P alone. The two empirical relationships, $r_1 = r_1' P^s$ and $r_1 = r''(1+\alpha P)$, are derived from $1/r_1 = 1/P \int_0^P dp/r$ by taking $r = r' p^s$ $(s < 1)$, and $r = r''(1+\alpha p)^2$, respectively.

If $r = r' p^s$

then $r_1 = (1-s) r' P^s$

i.e., $r_1 = r_1' \cdot P^s$ where $r_1' = (1-s) r' =$ constant.

If $r = r''(1+\alpha p)^2$

then $1/r_1 = 1/r'' \alpha P \cdot \{ 1 - \frac{1}{1+\alpha P} \}$

i.e., $r_1 = r''(1+\alpha P)$.

"Cloth Resistance".

If the resistance of a cloth with a cake upon it were merely equal to that of the clean cloth, we should always be able to neglect cloth resistance. Actually, however, the

very first layer of cake upon the cloth raises the resistance of the latter enormously. This can be understood by referring to the experiments of Hinchley, Ure and Clarke.[4] The equation for Cloth A in Fig.1, according to Underwood, is $dV/d\theta = P^2/.027$ i.e., $\rho_c' = .027$, while, if we plot $d\theta/dV$ vs. V and extrapolate to $V=0$, the intercept on the $d\theta/dV$-axis is ρ_c'/P, if we take equation (16) to represent their results. The average value of ρ_c' thus obtained is .125. Thus, even for coarse particles of magnesium carbonate, ρ_c' has been increased five times. Evidently, the first particles reaching the cloth embed themselves in the cloth fibres in such a way as to block up the cloth pores very considerably. The term for "cloth resistance" in a filtration equation, therefore, stands for the abnormally high resistance of these choked pores.

The effect of pressure upon the cloth resistance will be very largely a matter of the relative sizes of the cloth pores and of the particles. If the particle size is approximately the same as the pore-size, or larger, there will be a fairly definite boundary between cake and cloth, since it will be difficult for the particles to enter the cloth pores. As there are always small particles present, a certain amount of blockage will take place, so that "cloth resistance" will be higher than the resistance of a clean cloth, but it will behave similarly under pressure. In other words, if the pores are enlarged owing to pressure stretching the cloth between its

supports, so that the resistance of a clean cloth is proportional to $1/p^n$, then "cloth resistance" may be expected to be proportional to $1/p^n$. This was apparently the case in the experiments of Hinchley, Ure and Clarke, who used rigid, coarse, easily filtered particles.

Such particles are the exception in practice. It is much more usual to find particles are soft or very much finer than the pores in the filter cloth, and from such we should expect a very different behaviour. Such particles will pack into the pores and even in between the fibres of the cloth, so that it gets thoroughly stained with them. Twill and chain-weave cloths used by the present writer with ferric oxide developed a red stain which could not be scoured out. If increase of pressure causes the pores to enlarge, more particles will pack in, so that no decrease of cloth resistance will result, as would be the case with clean cloth resistance. On the other hand, such an intimate mixture of particles and of cloth-fibres should be subject to compression by deformation, just as is the cake, i.e., "cloth resistance" should behave in the same way as the resistance of a layer of a compressible cake.

In short, it is considered that equation (17), in which the cloth resistance per unit area, R_1, is given by $R_1 = R'/p^n$, applies only to the unusual type of slurry where the particles are coarse and rigid. In the great majority of cases, it is best to assume that the cloth behaves as a layer

of compressible cake, as was done in the derivation of equation (23), and, furthermore, as the particles plugged into the cloth are the same kind as those in the cake, it is reasonable to assume that the compressibility of the cloth is the same as that of the cake, or, at the most, differs but little from it.

Methods of Plotting.

Equations (21) or (24) can be considered as a fundamental form of filtration equation, which must be converted into various forms useful for interpreting experimental results. One value of such an equation is that it prevents a wrong analysis of results. This may be exemplified by the comparison of the log. V vs. log. θ plot and the θ/V vs. V plot for Almy and Lewis' results. Each plot gives a straight line within the limits of experimental error, but the two lines represent quite different equations. Each equation would be useful for calculating the effect of a slight change of conditions, but the one or the other would be seriously in error for a fairly large change of conditions. Such cases often arise when it is a question of designing a new plant to handle a given slurry, requiring a very different area of filtering surface and perhaps a different pressure and filter cycle.

In a filtration at constant pressure, we cannot apply full pressure immediately, since this would tend to plug

the pores of the cloth, and cause it to give an unduly high resistance. Furthermore, until sufficient cake has been deposited to cover the irregularities of the cloth-face, we may expect irregular effects, not allowed for in equation (24). Finally, in Appendix I., it is shown that, if cake and cloth are not equally compressible, we cannot be sure of the accuracy of equation (24) until $P_1/P_2 < 1$, i.e., until a cake has been deposited thick enough to equal in resistance the resistance of the cloth.

Constant pressure readings should not, therefore, be commenced until a volume, V_1, of filtrate has been collected, where V_1 is large enough to ensure a good covering of cake upon the cloth. Time readings can then be commenced and be carried on simultaneously with volume readings.

Then, if V_1 = volume of filtrate collected before time readings were commenced,

V' = volume of filtrate collected in time, θ, after time readings were commenced,

i.e., $V = V' + V_1$ = total volume of filtrate collected from the commencement of the run,

equation (24) becomes

$$dV'/d\theta = PA^2/\eta r_1 c(V'+V_1+V_0) \quad . \quad . \quad (25$$

Method (i) :- Integrating equation (25) at constant pressure, for which r_1 and V_0 are constants,

$$\theta = \eta r_1 c/2PA^2 . (V')^2 + \eta r_1 c/PA^2 . (V_1+V_0) . V'$$

$$= b(V')^2 + aV'$$

where $b = \eta r_1 c/2PA^2$ and $a = 2b(V_1+V_0)$

i.e., $\theta/V' = bV' + a$ . . (26

i.e., $d(\theta/V')/dV' = b$

θ/V' vs. V' should give a straight line with gradient, b, and intercept on the θ/V' -axis, a.

Then $r_1 = 2bPA^2/\eta c$ and $V_o = a/2b - V_1$

where b, P, A, η, c, a, V_1 are all known.

Method (ii) :- There is a second good method of analysing results, which, however, depends upon a knowledge of the value of V_o. We can write equation (25) as

$$d(V'+V_1+V_o)/d\theta = PA^2/\eta r_1 c(V'+V_1+V_o) \quad . \quad (27$$

Integrating at constant pressure,

$$\theta/\Delta(V'+V_1+V_o)^2 = b \quad . \quad . \quad (28$$

where $\Delta(V'+V_1+V_o)^2$ = increment of $(V'+V_1+V_o)^2$ in time, θ,

$$= (V'+V_1+V_o)^2 - (V_1+V_o)^2$$

$$= V'[V' + 2(V_1+V_o)]$$

There shall be occasion to choose between these two methods in the experimental work, so that the basis of choice will now be indicated.

Suppose that V' has been measured incorrectly, so that the true value is $V'+\delta$. Then the percentage error in V' is $\delta/V' \times 100$. Substituting the correct value in equation (26),

$$\theta = b(V'+\delta)^2 + a(V'+\delta)$$

$$\therefore \theta/V' = bV'(1+\delta/V')^2 + a(1+\delta/V')$$

i.e., neglecting the term in $(\delta/V')^2$, and substituting $a = 2b(V_1+V_o)$

$$\theta/V' = b[V' + 2\delta + 2(V_1+V_o)(1+\delta/V')]$$

$$\therefore d(\theta/V')/dV' = b[1 - 2\epsilon.\delta/V']$$

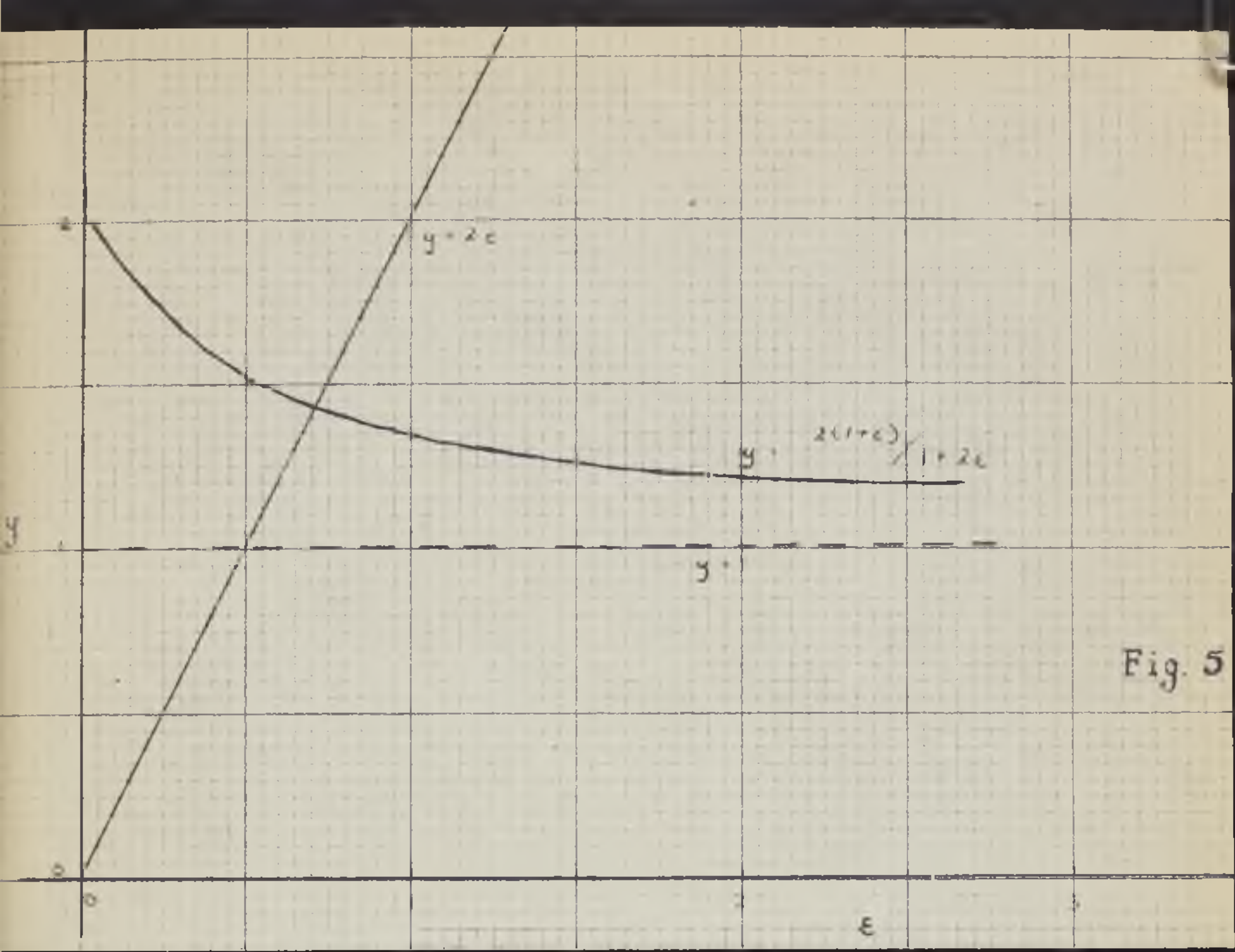


Fig. 5

where $\epsilon = {}^{V_1+V_0}/_{V'}$. This method of plotting gives a percentage error in b, 2ϵ times the experimental percentage error in V'.

Similarly, substituting the correct value of V' in equation (28),

$$\theta = b\,\Delta\,(V'+\delta+V_1+V_0)^2$$
$$= b\,(V'+\delta)\,[V'+\delta+2(V_1+V_0)]$$

Neglecting the term in δ^2,

$$\theta = b\,\{V'[V'+2(V_1+V_0)] + 2\delta(V'+V_1+V_0)\}$$

$$\therefore\ {}^{\theta}/_{\Delta(V'+V_1+V_0)^2} = b\left[1 + \frac{2(V'+V_1+V_0)}{V'+2V_1+2V_0}\cdot {}^{\delta}/_{V'}\right]$$
$$= b\left[1 + {}^{2(1+\epsilon)}/_{1+2\epsilon}\cdot {}^{\delta}/_{V'}\right]$$

so that the percentage error in b is here ${}^{2(1+\epsilon)}/_{1+2\epsilon}$ times the experimental percentage error in V'.

In Fig.5 are plotted $y = 2\epsilon$ and $y = {}^{2(1+\epsilon)}/_{1+2\epsilon}$ against ϵ, and the dotted line gives $y = 1$, i.e., when the percentage error in b equals the percentage error in V'. From this, Method (i) is seen to be a poor method when $\epsilon > 1$, i.e., when $V' < V_1+V_0$. This method should, therefore, be used only when V_1 and V_0 are small, and V' is large. Moreover, it is preferable to obtain several values of V' and of θ, to plot ${}^{\theta}/_{V'}$ vs. V', and to draw an average line through the points, in order to reduce the percentage error in V' to a minimum.

Method (ii), on the contrary, gives a more accurate value of b when ϵ is great, i.e., when V_1 and V_0

are large and V' is small. Further, as this method does not magnify the percentage error in b appreciably for any value of ε, we need not plot points, but can calculate b from $\theta/\Delta(V'+V_1+V_o)^2 = b$, directly. Method (ii) is undoubtedly the better method, except that it depends upon the knowledge of the value of V_o. Suppose the value of V_o were in error, the true value being $V_o + \delta_o$. Then

$$\theta = b\,\Delta\,(V' + V_1 + V_o + \delta_o)^2$$

$$= b\,V'\left[V' + 2\,(V_1 + V_o + \delta_o)\right]$$

i.e., $$\theta/\Delta(V'+V_1+V_o)^2 = b\left[1 + 2\delta_o/V'+2V_1+2V_o\right]$$

$$= b\left[1 + \delta_o/(V_o + V+V_1/2)\right]$$

The error is serious when $V+V_1/2$ is small, especially when V_o is large and uncertain in value. When, however, $V_1+V/2$, which is the mean value of the volume of filtrate before and after the run, is large, the error is small.

The distinction between these methods of analysis will be very important later, in the discussion of "mixed pressure" experiments. Suppose that, in a single experiment, we start at a pressure of 25 lbs./sq.in., wait until cake formation has fairly started, and then commence to take readings of θ and of V' for several minutes at this pressure. The pressure is then changed to 50 lbs./sq.in., and a new set of readings is taken at this pressure. At the lower pressure, the value of V_o is unknown, so that Method (i) must be used. Since, however, $V_1 + V_o$ is small and V'

reaches comparatively high values, this method should give good results. Both r_1 and V_o can be obtained from the straight line given on plotting θ/V' vs. V'. At the higher pressure, we have reached a high value of V_1, while V' has to start from zero once more. Method (i) would be likely to yield a most inaccurate result. Under these conditions, however, Method (ii) gives its greatest accuracy, and, since the value of V_o has now been determined, this method can be used. To assume that V_o remains unchanged at the higher pressure is probably not quite true, especially since Hinchley, Ure and Clarke[4] have shown that the resistance of clean cloths decreases considerably at higher pressures. As has been pointed out in the previous section, however, a clean cloth behaves differently from a cloth with a cake upon it, for the resistance of the latter is due mainly to cake material embedded in its pores, and is subject, therefore, to the same laws as is cake resistance. As shown in Appendix I., V_o depends upon the ratio, R_1/r_1, and is not, therefore, independent of pressure unless cake and cloth have the same compressibility. It is doubtful if the difference in compressibility is ever very marked, so that, if unclogged cloths are used to reduce the value of V_o as much as possible, any errors due to errors in V_o should be negligible, especially since, by using Method (ii) for analysis at the higher pressure stage of the experiment, errors in V_o tend to be masked by the high

value of $V+V_1/2$.

Scope of Experimental Work.

According to equation (24),

$$dV/d\theta = PA^2/\eta r_1 c (V+V_0)$$

derived from the assumption that the compressibility of a cake is due to the deformation of the particles within it, the specific resistance, r_1 , depends upon the value of the pressure of filtration, P , alone. It should be independent of the concentration of the slurry, c , of the area of the filtering surface, A , and of the viscosity of the filtrate, η . Table I., in which is summarised the range of the more reliable, published investigations, shows that these are too incomplete to establish the general validity of equation (24). It should be further tested along the following lines;

(i) A wider range of pressures is needed. Hinchley, Ure and Clarke[4], and Gilse, Ginneken and Waterman[8] used suction filters, so that their pressures of filtration do not rise above 14 lbs./sq.in. Almy and Lewis[2] varied their pressures between 5 lbs./sq.in. and 100 lbs./sq.in., but did not vary any other conditions.

(ii) A more complete study of the effect of concentration is needed, as the experiments of Gilse, Ginneken and Waterman provide the only data for the effect of concentration upon a compressible cake.

(iii) The area of the filtering surface, A ,

TABLE I. Summary of the More Important Studies on the Rate of Filtration.

Workers	Material	Number of Experiments.	Range of Pressures. (lb./sq.in.)	Range of Concentrations, in kg./litre.	Remarks.
Almy & Lewis	Chromium Hydroxide	6.	5 - 100	-	Very compressible cakes. Used 6" plate and frame filter press. No room temperatures recorded.
Hinchley, Ure & Clarke.	Calcium Carbonate	10.	-	.011 - .128	All ideal cakes. Used small suction leaf filter.
	Barium Phosphate	5	-	.021 - .123	No room temperatures recorded.
	Magnesium Carbonate	2	5.5 - 13.2	-	
	Calcium Carbonate	2	5.5 - 13.2	-	
	Barium Phosphate	2	5.5 - 13.2	-	
Gilse, Ginneken & Waterman	Activated Carbons.	32	1.42 - 10.	.007 -.0005	Moderately compressible cakes. Used small suction filter of .4534 sq.dm. area of filtering surface. All experiments performed at 20°C.

should be changed, as there is only one experiment of the kind, published by Gilse, Ginneken and Waterman.

(iv) The viscosity of the filtrate should be altered. Almy and Lewis alone have published two experiments for small changes of viscosity. Apart from Gilse, Ginneken and Waterman, indeed, no workers have insured that room temperature was constant, so that their data are subject to unknown errors, resulting from changes in room temperature, which would alter the viscosity of the filtrate.

(v) A wide variety of cakes, ranging from ideal to very compressible, should be studied, to find if equation (24) applies for all of them. In particular, the relation between r_1 and P is of interest. It appears that there is no general relationship between them, for $r_1 = r_1' P^s$ holds true for the data of Almy and Lewis on chromium hydroxide, and $r_1 = r''(1+\alpha P)$ for the data of Gilse, Ginneken and Waterman on activated carbons.

If equation (24) is correct, the above lines of work should establish that r_1 is independent of c, A, η. It should also be independent of the way in which the cake was formed. In the derivation of equation (24), no stipulation was made that the cake be formed at a pressure, P, as it is in a constant pressure filtration. Equation (24) should, therefore, be true for a given thickness of cake, whether it be deposited wholly at a pressure, , or whether it be

(formed at a

lower pressure which is afterwards raised to the value of P.

(vi) This point will be tested in "mixed pressure" experiments.

Again, in the theory of compressible cakes, it was pointed out as implicit in Underwood's theory that r_1 is a function of the absolute pressure, $P_t = P + P_b$, in the filter press, where P = pressure of filtration = pressure difference across cake and cloth, and P_b = absolute pressure on the filtrate side of the cloth, i.e., that r_1 is dependent both upon P and upon P_b. In the theory used to derive equation (24), r_1 is dependent upon P and independent of P_b.

(vii) If the same value of P be used in a vacuum filtration and in a positive pressure filtration, i.e., using values of P_b of (14.7 - P) lbs./sq.in. and of 14.7 lbs./sq.in respectively, the value of r_1 should be greater in the latter experiment according to Underwood's theory, and should remain unchanged according to the theory of particle deformation.

The remaining lines of experiment will be described later.

II. E X P E R I M E N T A L.

The aims of the following experimental work have been to test equation (24) as thoroughly as possible, and to prove the truth of the new theory for compressible cakes.

Apparatus.

In order to obtain complete control of experimental conditions, and to be able to reproduce them accurately, it is necessary to use small-scale apparatus, as has been observed by Gilse, Ginneken and Waterman.[8] It is, furthermore, a waste of materials to use large-scale apparatus, if the chemicals to be used are fairly dear.

The present apparatus was therefore designed to give about a litre of filtrate in a single exeperiment. The vessel containing slurry has a capacity of about 1.6 litres, and the area of the filtering surface is .342 sq.dm.

In the present work, materials of a corrosive nature were little used, but , when this work is extended, it is probable that such substances will be used, so that the slurry-containing vessel was made of copper. The filter was cast from Admiralty bronze, and the castings turned to shape. This bronze is fairly resistant to corrosion, and does not give a porous casting. Fig.6 gives a sectional view of the filter as ordinarily set up. It is really a Buchner filter, made of metal, and modified for the application of high

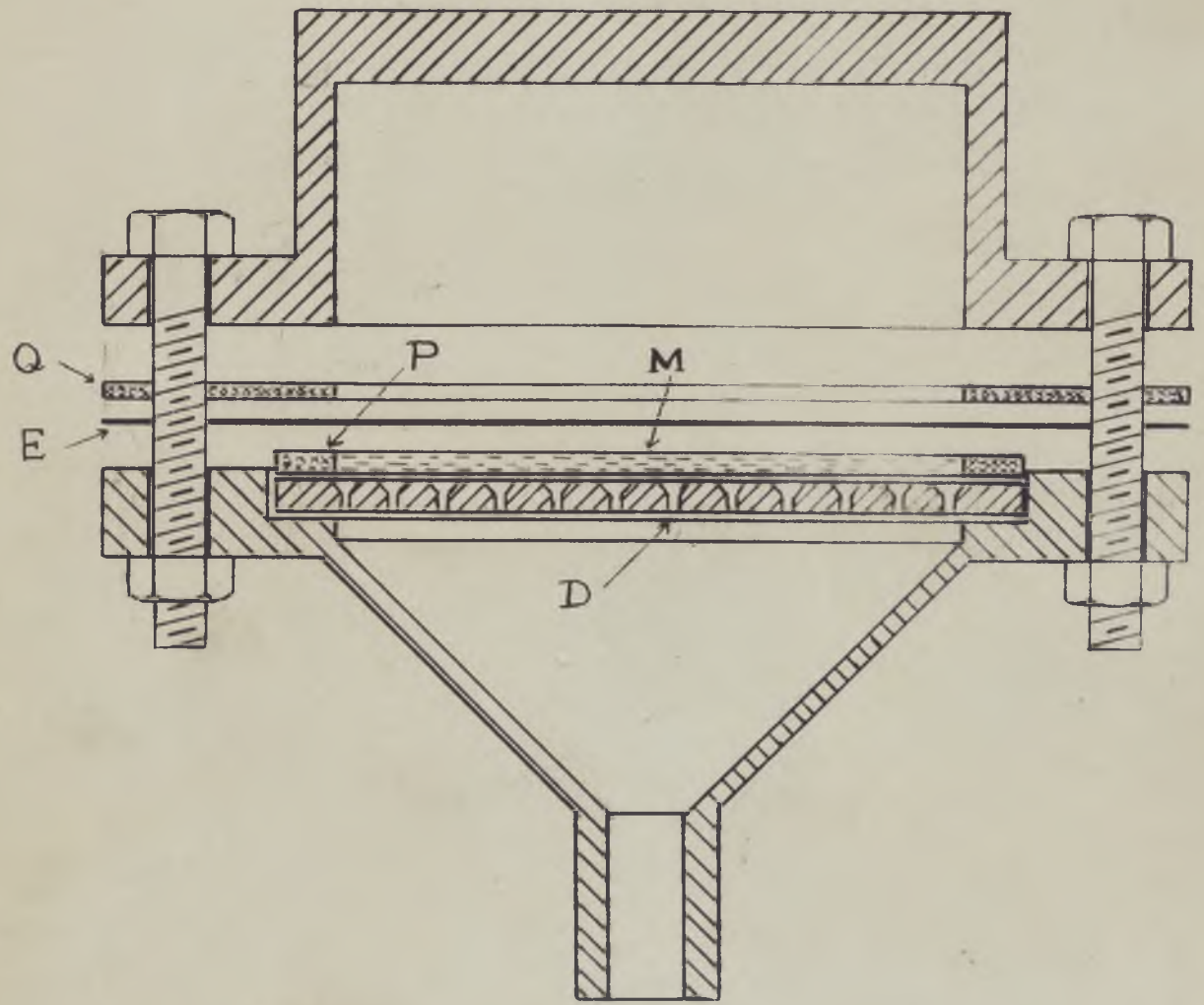


Fig. 6

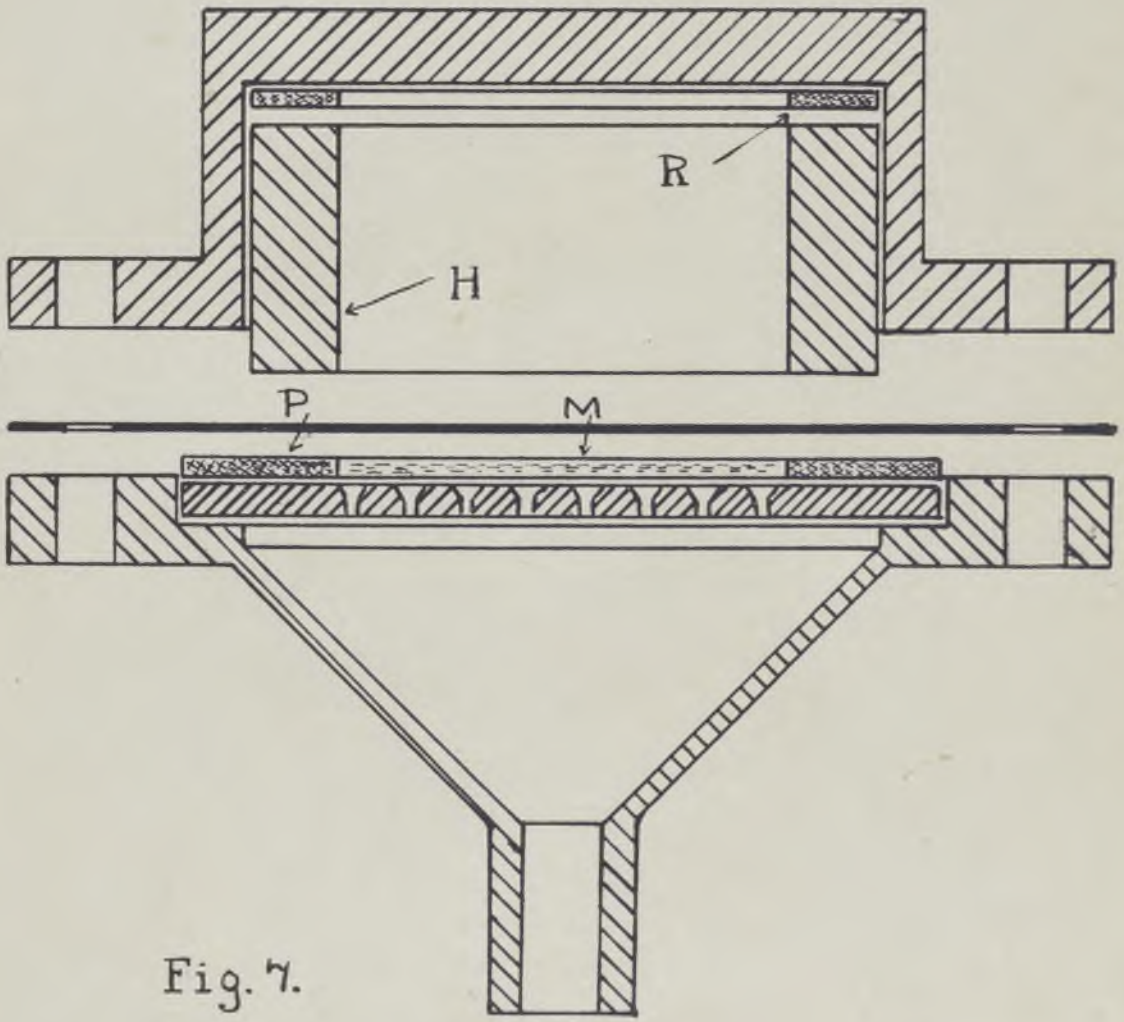


Fig. 7.

positive pressures of filtration, and for ease of dismantling and assembly. Apart from the body of the filter, there are a perforated base-plate, D , a packing, P , three layers of copper gauze, M , a filter-cloth, E , and a second packing, Q. To maintain exactly the same area of filtering surface each time, it is necessary to cut the packing, P , very accurately and to use a hard packing such as asbestos steam packing, which will not change shape in use. The packing, Q , was found necessary for vacuum filtrations. It also had to be cut accurately, and, as it was a rubber-insertion packing, it had to be renewed fairly often. This did not matter much, however, as the vacuum filtrations were only a small proportion of the whole. The copper mesh is to keep the cloth from the base-plate, since the blank spaces between the holes would block off part of the surface of the cloth and tend to give too low an effective area in the early stages of the filtration. The mesh also prevents the cloth sagging into the hollow space left by the packing, P. In Fig.7, a similar sectional view of the filter is shown, fitted to filter with half the previous area. This is effected by introducing a bronze cylinder, H , fitting closely into the filter as shown, together with a rubber-insertion packing, R , and by modifying the packing, P , and the copper gauze, M , to correspond.

Fig.8 gives a photograph of the various parts of the filter, F , and Fig.9, a photograph of the whole layout.

Fig.8a.

Photograph of stirrer.

Fig.8b.

Body of filter, showing connections, packing, drainage plate, and copper gauze.

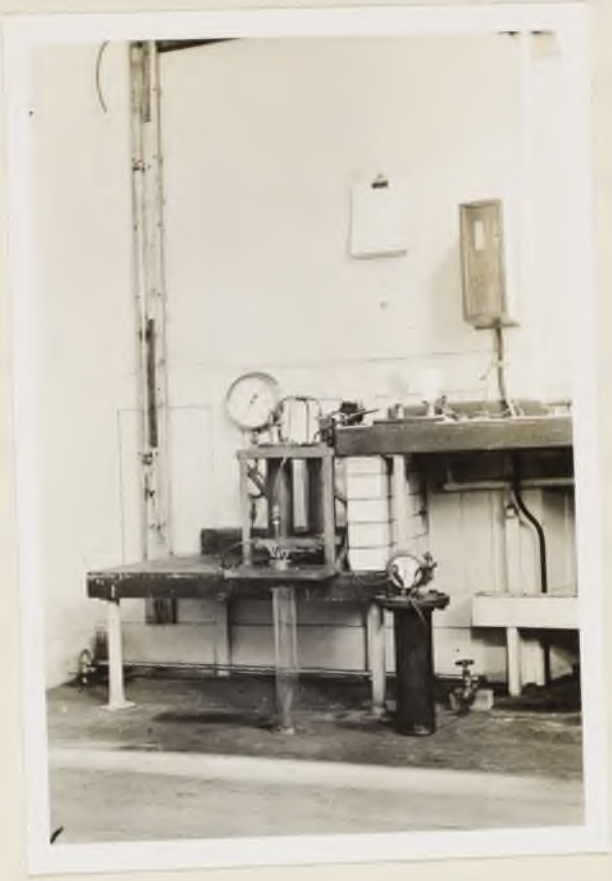


Fig.9a

Apparatus arranged for
positive pressure filtration.

Fig.9b.

Apparatus arranged for
vacuum filtration.

Fig.10 presents a diagrammatic view of the whole apparatus, as used for positive pressure filtrations. A and B are vessels of 1.6 litres capacity each, A for suspensions and B for clean water. A is provided with a stirrer, S , driven by a 1/75 H.P. electric motor. A small propeller on the end exerts a downward thrust, and, as the stirrer is placed eccentrically in the vessel, a very efficient agitation is obtained. This is a prime necessity, since, if the slurry be allowed to settle, the experimental readings will be useless. Dotted lines indicate the compressed air connections for applying pressure, and full lines indicate the passage of slurry and of wash-water to the filter, F. The needle valve, N , controls the admission of compressed air, and hence the pressure of filtration. The pressure gauge, G , measures directly the pressure drop through cake and cloth. To carry out a filtration, cocks, C_1 , C_3 , C_5 are shut and C_2 , C_4 opened, and, to wash the cake, C_2 , C_4 , C_5 are shut, and C_1 , C_3 opened. To empty the filter, F , of liquid, C_1 , C_2 , C_3 , C_4 are shut and C_5 opened.

G is a Bourdon type of pressure gauge, with an 8" diam. dial and scale reading from zero to 150 lb./sq.in., i.e., a working scale of 10 lb./sq.in. to 100 lb./sq.in. It was found, on calibration, to give readings accurate to within .5%, above 20 lb./sq.in. For experiments below 20 lb./sq.in., which includes all vacuum filtrations, a mercury U-tube manometer was used.

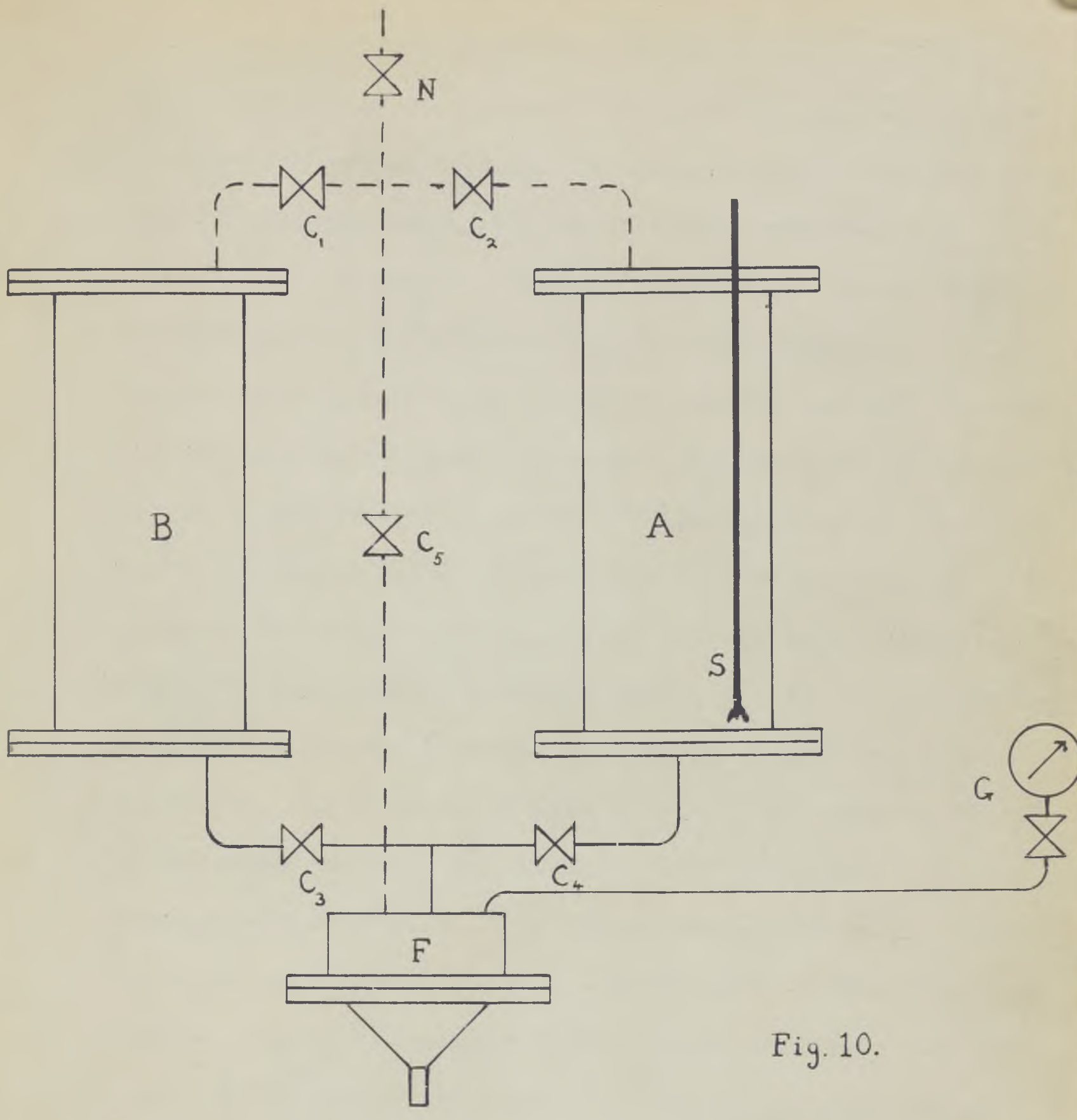


Fig. 10.

In Fig.11 is given a diagrammatic view of the layout for vacuum filtration. In this case, the vessel, B , is used as a vacuum receiver, wash-water being dispensed with, and the pressure gauge, G , is therefore attached to B, as shown. Cocks, C_2 and C_3 are kept permanently closed, while C_6 is left open to the atmosphere. The needle valve, N , communicates with a large evacuated vessel, and thus controls the pressure in B , and, therefore, the pressure of filtration. T_1 and T_2 are two-way taps, connecting the conical flasks, V_1 and V_2 , respectively, to N one way, and to atmospheric pressure the other way; and K is a two-way cock, delivering filtrate either to V_1 or to V_2. Cocks, C_1 , C_4 , C_5 , C_6 remain open during the whole of the experiment. Initially, T_1 and T_2 connect V_1 and V_2 to B, so that V_1 and V_2 are both evacuated to the pressure in B, and K delivers filtrate to V_1 . After a given interval of time, K is turned to deliver to V_2 , and T_1 is turned to allow air into V_1 , which is then removed and emptied into a measuring cylinder. V_1 is replaced, and T_1 is turned to connect it once more with B, and, at the end of another interval of time, K is turned to deliver to V_1 , while V_2 is emptied and replaced in a similar manner. The same operations are repeated till the end of the experiment. It is to be noted that the manometer is connected to the filter, F , as well as to B, for the pressure in the filter is greater than atmospheric pressure by an amount equal to the pressure

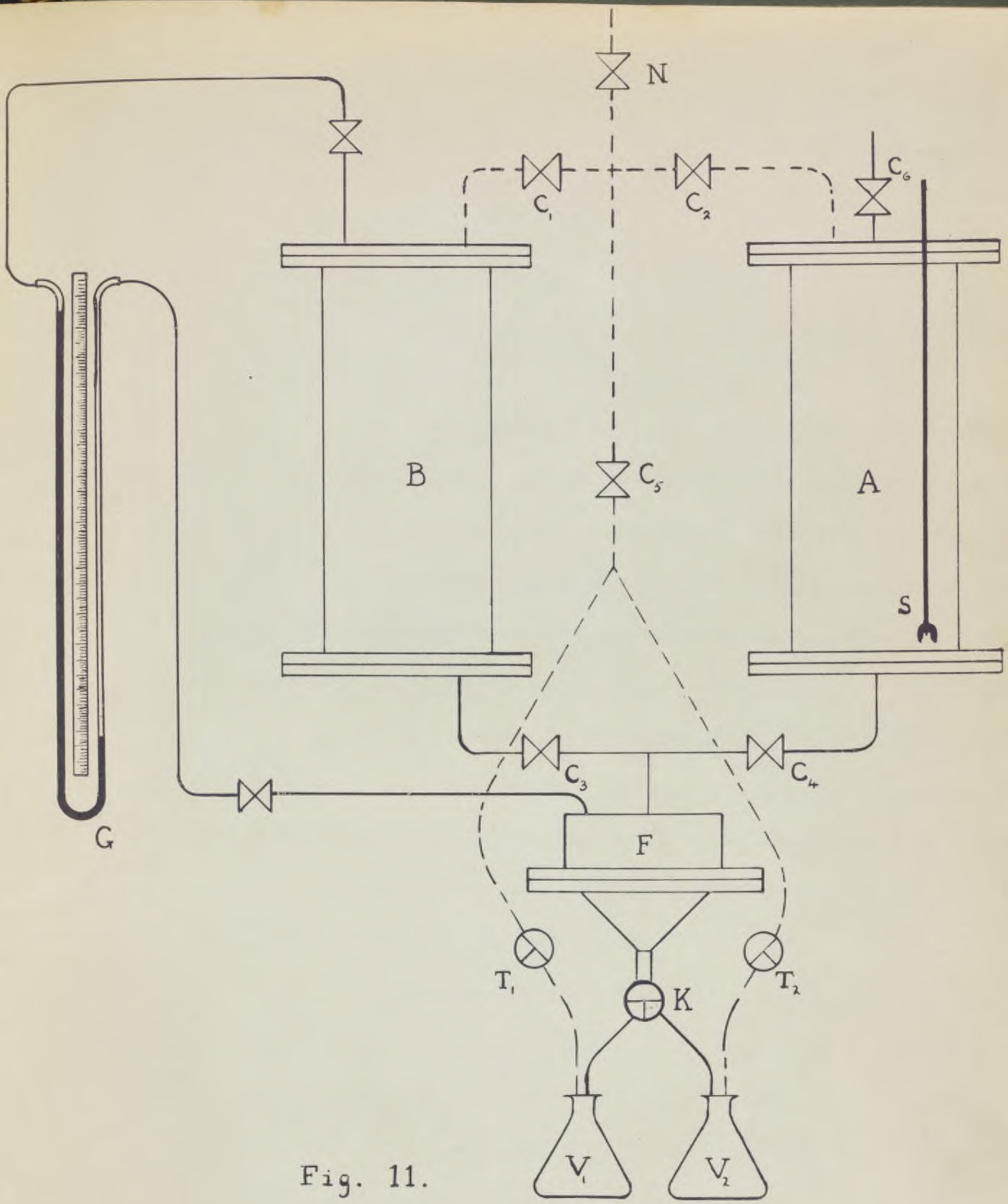


Fig. 11.

due to the head of slurry in A. Arranged as shown in the diagram, G measures pressure difference across cake and cloth, i.e., pressure of filtration.

Technique.

Time is measured with a stop-watch, and provides the most accurate of all the readings.

Volumes are measured by collecting the filtrate in 60 - 100 ml. beakers, changing these at given intervals of time, pouring into a 250 ml. measuring cylinder, and emptying this in turn whenever the 200 ml. mark is passed. The measuring cylinder is accurate, so that the error should not exceed one or two mls. in each 200 mls., i.e., about 1%.

Pressures are controlled by the needle valve, N , which has to be manipulated during the whole of the experiment. For pressures above 25 lb./sq.in., the error should not exceed 1%, and, for higher pressures, is probably within the error of the instrument itself, ½%.

The temperature of the filtrate is taken at the beginning and at the end of the experiment. If it changes by more than .5°C, the experiment is discarded. Where distilled water is used, the viscosity can be found from tables, and should be accurate within 1%.

Where the filtrate is not distilled water, the viscosity is measured with an Ostwald viscosimeter at the temperature of the experiment.

The possible error from these sources can, therefore amount to 3% or 4%, but, in practice, a 2% accuracy is to be expected.

The main source of error in filtration experiments is settling, either in the slurry-container, or in the filter. This is mainly a question of the time of filtration, so that every endeavour is made to carry out the experiment quickly, preferably within 20 minutes, if a cake of sufficient thickness can be formed in this time. Furthermore, the amount of filtrate collected is always less than 1 litre, out of the 1.5 litres of slurry charged into the slurry vessel; for settling in the slurry-vessel will be a cumulative effect, and it will be greatly magnified when the volume of slurry remaining is only about 1/3 of the original amount.

When an experiment is finished, the filter, the slurry-vessel, and the leads to the pressure gauge are washed out, and assembled for another filtration.

Choice of Materials.

The substances first chosen were ferric oxide, in the finely-ground form used as a pigment, calcium carbonate in the form known as whiting, and kieselguhr. The basis of choice was that, in the massive form, these substances are rigid, and that none of them are acted upon by water. Kieselguhr, owing to its rigid particles, and its comparatively coarse state of division, is well known to give ideal cakes. Whiting, though

another rigid material, is much more finely-divided, and gives a slightly compressible cake; while ferric oxide is still more finely-divided, and correspondingly more compressible.

It might be expected that fine particles derived from rigid materials should give ideal cakes, or, as they are more usually termed, incompressible cakes, since the incompressibility of such cakes depends on the resistance to change of shape and of size of the particles in them. This is not, however, always true, for Gilse, Ginneken and Waterman[8] have shown cakes of activated carbons are compressible. They considered that this was due to the squeezing out, under pressure, of a stationary layer of water adsorbed on the surface of the particles. Finely-divided ferric oxide, as will be seen shortly, also gives a compressible cake, and, in this case, it is believed that part of the ferric oxide is colloidal in nature, and that this material coagulates in flocs, which act as deformable particles within the cake.

Kieselguhr and whiting slurries are obtained by stirring the particles into suspension in water, and the results given by these slurries are easily reproducible. The cakes are, however, too nearly ideal for testing equation (24). Ferric oxide, which gives a distinctly compressible cake, was, therefore, chosen for the first part of the investigation. It was hoped that it, too, could be suspended in water to give reproducible slurries. It was soon found, though, that, as a

substantial portion proved fine enough to form a colloidal suspension, it was very susceptible to coagulation by electrolytes. The commercial oxide had, therefore, to be washed free from electrolytes by a tedious series of decantations with distilled water; and all slurries for experimental work were prepared by suspending this washed oxide in distilled water.

In all, three stocks of this washed ferric oxide were prepared. These were not, however, identical, though all prepared from the same original sample of commercial ferric oxide. During the lengthy process of washing by decantation, a certain amount of the most finely-divided material refused to settle and was therefore lost. The coarsest particles were deliberately settled out and rejected, since they would have tended to cause errors by settling out during filtration. As the percentage of rejected particles, both fine and coarse, would be different for each case, the size distribution of the particles in each stock would be different.

At a later date, a certain refined clay was found to be very suitable for these experiments. The cake obtained from it was much more compressible than that from ferric oxide; it gave reproducible slurries without any of the troubles given by ferric oxide, and the slurries were not too quick in settling. It proved, thus, to be an admirable substance for tesing equation (24).

The remaining materials chosen were three metallic hydroxides, magnesium hydroxide, aluminium hydroxide, and ferric hydroxide, chosen because they are gelatinous and give slimy, highly-resistant, highly-compressible cakes, and, therefore, provide a good test for the general applicability of equation (24). The origin of the magnesium hydroxide will be described later. The others were produced by adding strong sodium hydroxide solutions to strong solutions of aluminium sulphate and ferric chloride, respectively, till neutral to litmus.

In all three cases, the hydroxides were washed free from soluble electrolytes by decantation with distilled water. This had a two-fold purpose. First, for reproducibility, as portions of the stock slurry must be diluted with distilled water to make up slurries for the experiments, the stock, itself, should be a suspension in distilled water. Second, it is preferable to use suspensions in distilled water for all experiments because such suspensions settle much more slowly than do those in which soluble electrolytes are present. So marked, indeed, was the decreased rate of settling in distilled water that, in the washing process, the final decantations were performed in a centrifuge, since settling under gravity was taking too long. A slow settling rate is particularly of importance for such substances, since, as they give such very highly-resistant cakes, experimental runs last one and two

hours, and even more.

Experimental Results.

It has already been shown that, when cloth resistance is unknown, the most satisfactory method for testing equation (24) is to use the plot of θ/V' vs. V', which should be linear, according to $\theta/V' = bV' + a$

where $b = \eta r_1 c/2PA^2$ i.e., $r_1 = 2bPA^2/\eta c$

and $a = 2b(V_1 + V_0)$ i.e., $V_0 = a/2b - V_1$

The graphs of θ/V' vs. V' for the first series of twelve experiments, with Stock A of ferric oxide, are shown in Figs.12, 13, 14. In every case, there is close approximation to a straight line.

Table II. summarises the pressures of filtration, P, the concentrations of the slurries, c, the viscosities of the filtrates, η, the values of a and of b, the values of V_1, the values of V_0 and of r_1, calculated as above, and, finally, the values of r_1, calculated from $r_1 = \cdot 98 . P^{\cdot 41} \times 10^6$. The area of the filtering surface has a constant value of .342 sq.dm. All calculations are on the basis of the decimetre-kilogram-second system of units, in which the unit of volume is the litre, and the unit of viscosity (100 poises) is the centipoise. Since P has been measured in lb./sq.in., it is necessary to convert it into kg./sq.dm. by multiplying by the factor, 7.05, i.e., $r_1 = \frac{bP}{\eta c} \times 2 \times 7.05 \times (.342)^2 = \frac{bP}{\eta c} \times 1.65$.

Inspection of Table II shows that, at each value

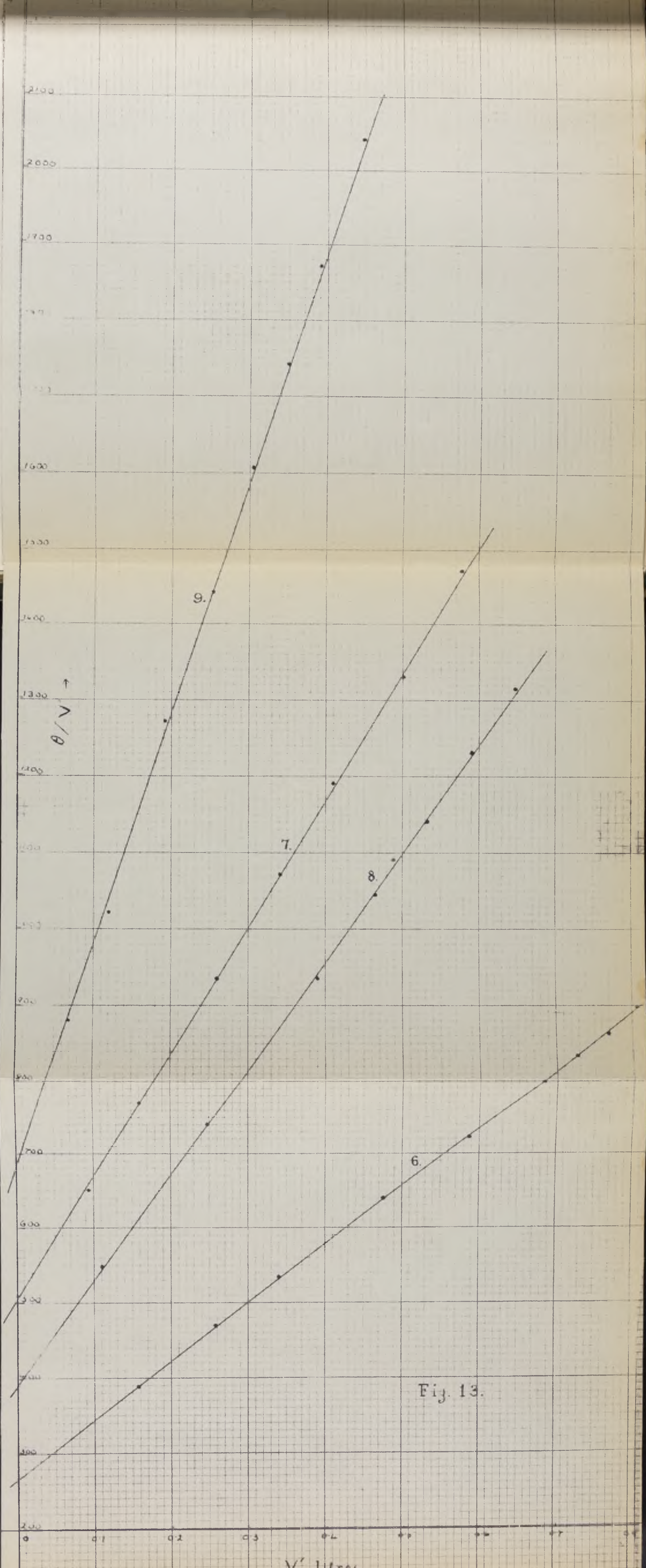


Fig. 13.

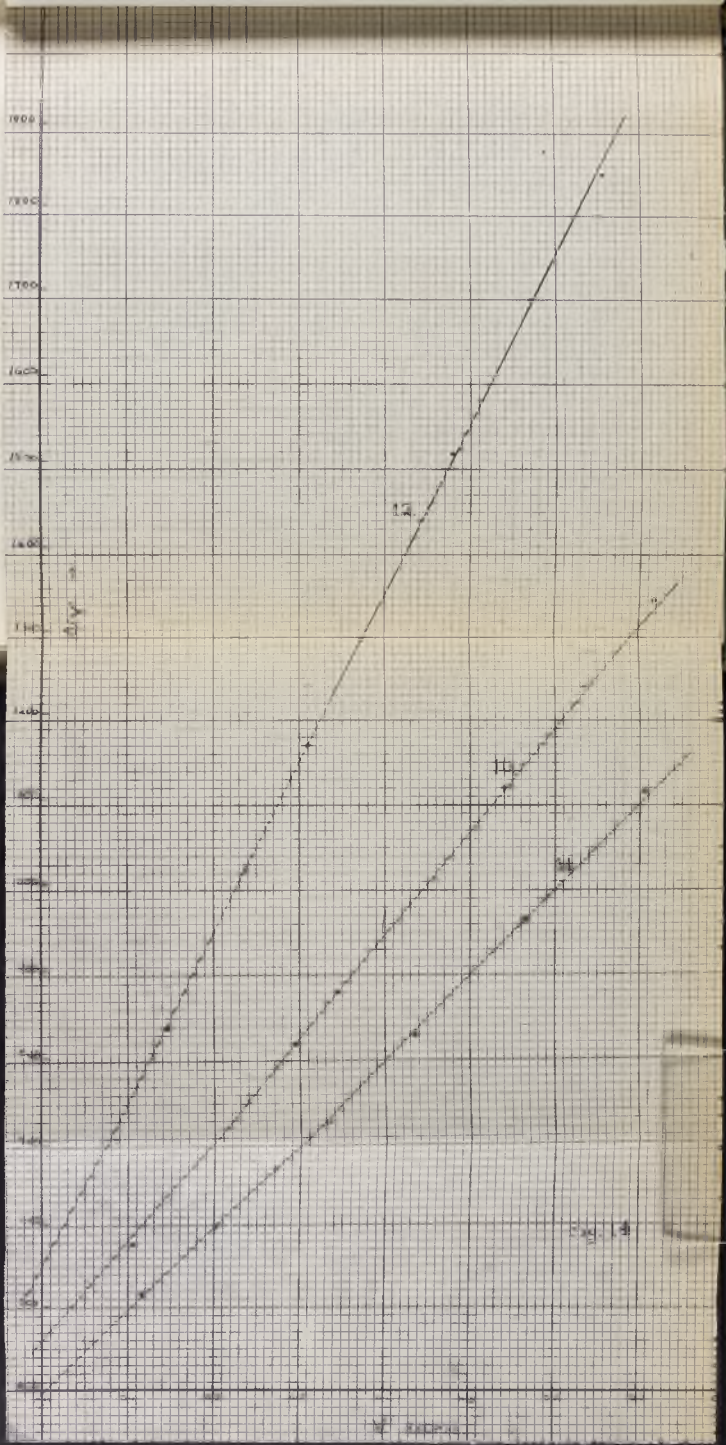


TABLE II. Experiments with Stock A of Ferric Oxide.

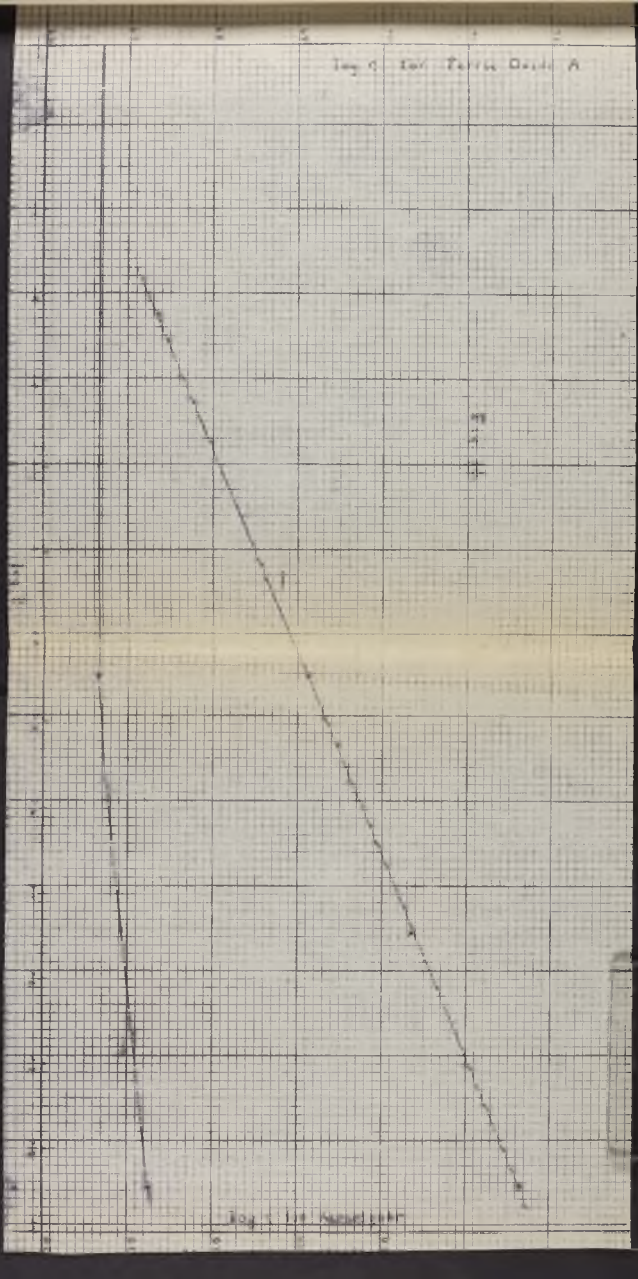
Area of Filtering Surface = .342 sq.dm.

Expt.	P in lb. sq.in.	c in kg. litre of filtrate	η in centipoises	a	b	V_1 in litres	V_0 in litres	r_1 in $\frac{(\text{sec.})^2}{\text{kg.}} \times 10^{-6}$	$.98\,P^{.41}$ (P in kg. sq.dm.)
1.	9.4.	.0051	1.24	1000	2220	.030	.195	5.45	5.47
2.	9.4	.0051	1.14	984	2000	.053	.192	5.35	5.47
3.	25.	.005	1.14	620	1125	.030	.246	8.15	8.17
4.	25.	.0101	1.24	640	2500	.045	.083	8.25	8.17
5.	25.	.0101	1.20	515	2380	.053	.055	8.1	8.17
6.	50.	.0052	1.15	265	785	.155	.014	10.8	10.8
7.	50.	.0100	1.29	505	1680	.080	.051	10.75	10.8
8.	50.	.0099	1.11	390	1430	.090	.046	10.75	10.8
9.	50.	.0200	1.16	680	3060	.062	.050	10.9	10.8
10.	75.	.0100	1.20	460	1215	.104	.085	12.5	12.8
11.	100.	.0100	1.14	395	1005	.147	.050	14.5	14.4
12.	100.	.0201	1.13	550	2000	.120	.018	14.5	14.4

of the pressure of filtration, P, there is a single value of the specific resistance, r_1, independent of the variations in concentration and in viscosity. The variations of viscosity, depend-ing, as they did, merely on changes of room temperature, are not sufficient to establish the validity of the viscosity term in equation(24); but they do indicate that it serves as a useful correcting term for such variations. For example, in Expts.7 & 8, the same value for r_1 is obtained for viscosities of 1.29 and 1.11 centipoises, respectively.

If log. r_1 be plotted against log. P, as in Fig.15, a straight line is obtained, of gradient, .41, corresponding to $r_1 = \cdot 98 P^{\cdot 41} \times 10^6$, where P is in kg./sq.dm.. The comparison btween the observed values of r_1 and of those calculated from this equation is given in the last column of Table II., and shows that there is no regular deviation within the range of pressure used.

For experiments 4,5,9, the data in Table II. represent the first part of each experiment only, carried out at constant pressures of 25, 25 & 50 lb./sq.in., respectively, In Expt.4, time readings were commenced at 25 lb./sq.in., when $V_1 = .045$ litre, and continued until $\theta = 1340$ secs., and $V' = .606$ litre, i.e., $V = V' + V_1 = .651$ litre. The graph of θ/V' vs. V', as already shown, gives $r_1 = 8.25 \times 10^6$ and $V_0 = .083$ litre. Time readings were then recommenced one minute later at 75 lb./sq.in., when V had risen to .677



litres, which gave the new value of V_1, and were carried on until θ = 420 secs. and V' .194 litres. It was shown earlier that the most suitable analysis for this part of the experiment is

$$\theta / \Delta(V' + V_1 + V_o)^2 = b$$

Now, $\Delta(V' + V_1 + V_o)^2 = (.194 + .677 + .083)^2 - (.677 + .083)^2$

$= .322$ litres^2

so that $b = 420/.322 = 1265$

and $r_1 = 1265 \times 75 \times 1.65 / 1.24 \times .0101$

$= 12.5 \times 10^6$ (secs.)^2/kgs.

In practice, the data were presented in the following form;

θ	V'	V_1+V_o	$V+V_o$	$(V+V_o)^2$	$\Delta\theta/\Delta(V+V_o)^2 = b$
0	.000	.760	.760	.578	
60	.031	.760	.791	.626	$60/48 \times 10^3 = 1250$
180	.089	.760	.849	.721	$120/95 \times 10^3 = 1265$
300	.143	.760	.903	.815	$120/94 \times 10^3 = 1275$
420	.194	.760	.954	.910	$120/95 \times 10^3 = 1265$
					Average = 1265

i.e., a series of values of b is obtained, and r_1 is calculated from the average value of b.

Similarly, in Expt.5, the pressure of filtration was changed from 25 lb./sq.in. to 50 lb./sq.in., and then to 100 lb./sq.in.; and, in Expt.9, from 50 lb./sq.in. to 100 lb./sq.in. Table III. summarises the results, showing the values of r_1 obtained in this way, the average values of r_1 in Table II, and the values of r_1 calculated from $r_1 = \cdot 98 P^{\cdot 41} \times 10^6$. The agreement is sufficient to establish that, for a given value of P, r_1 has the same value in a mixed pressure

TABLE III. "Mixed-pressure" Experiments with Stock A of Ferric Oxide.

Expt.	P in lb./sq.in.	$r_1 \times 10^{-6}$ (for expt.)	$r_1 \times 10^{-6}$ (average value in Table II.)	$.98\,P^{.41}$ (P in $\frac{kg.}{sq.dm}$)
4.	25.	8.25	8.17	8.17
	75.	12.5	12.5	12.8
5.	25.	8.1	8.17	8.17
	50.	10.75	10.8	10.8
	100.	14.5	14.5	14.4
9.	50.	10.9	10.8	10.8
	100.	14.6	14.5	14.4

experiment, in which part of the cake has been deposited at a pressure lower than P, as it has in a single pressure experiment, in which the pressure has been maintained at the value of P throughout.

This is in agreement with the theory of particle deformation. According to this theory, if the difference of pressure across a cake be P, r_1 is given by $1/r_1 = 1/P \int_0^P dp/r$, where r is a function of p, i.e., r_1, at any given moment, is dependent solely upon the value of P at that moment, and is unaffected by any previous smaller value of P.

This method of "mixed pressures" has a practical as well as a theoretical sifnificance, for it provides a technique whereby two or more values of r_1 may be obtained in a single experiment. This is useful in the industrial laboratory, where the relationship of r_1 to P is necessary to determine the most economical pressure of filtration, and where speed, and simplicity of apparatus are essential.

A similar series of experiments was now conducted with each of the Stocks B and C of washed ferric oxide. The results are summarised in Tables IV. and V., respectively, the complete data for mixed-pressure experiments being here included, as they are in all the tables which follow. The values of r_1 in the final columns are calculated from $r_1 = 3{\cdot}2\,P^{\cdot 16} \times 10^6$ for Table IV., and from $r_1 = 2{\cdot}08\,P^{\cdot 25} \times 10^6$ for Table V., where P is in kg./sq.dm. In both cases, the experimental

TABLE IV. Experiments with Stock B of Ferric Oxide.

Area of Filtering Surface = .342 sq.dm.

Expt.	P in lb./sq.in.	c in kg./litre	η in centi-poises	V_o in litres	r_1 in $\frac{(\text{sec.})^2}{\text{kg.}} \times 10^{-6}$	$3.2\,P^{.18}$ (P in kg./sq.dm.)
1.	9.4	.005	1.02	.060	6.85	6.8
	25.	"	"	"	8.2	8.1
	50.	"	"	"	9.3	9.2
2.	9.4	.005	1.11	.064	6.75	6.8
	25.	"	"	"	8.0	8.1
3.	14.4	.005	.98	.133	7.5	7.65
	25.	"	"	"	8.15	8.1
	40.	"	"	"	8.75	8.85
4.	25.	.005	1.06	.027	8.25	8.1
5.	25.	.010	1.06	.027	8.2	8.1
6.	25.	.010	.95	.076	8.3	8.1
	50.	"	"	"	9.2	9.2
	100.	"	"	"	10.5	10.4
7.	25.	.020	.94	.001	8.2	8.1
8.	40.	.0025	.97	.163	8.85	8.85
9.	40.	.0025	1.09	.239	8.85	8.85
10.	50.	.010	.96	.032	9.35	9.2
11.	50.	.010	.95	.021	9.4	9.2
12.	100.	.020	.98	.007	10.35	10.4
13.	100.	.020	.94	.010	10.25	10.4

TABLE V. Experiments with Stock C of Ferric Oxide.

Expt.	P in lb./sq.in.	C in kg./litre	η in centi-poises	A in sq.dm.	V_o in litres	r_i in $\frac{(sec.)^2}{kg.} \times 10^{-6}$	$2.08 P^{.25}$ (P in kg./sq.dm.)
1.	4.7	.0025	1.02	.342	.073	5.05	5.0
	9.4	"	"	"	"	5.85	5.95
	14.1	"	"	"	"	6.7	6.8
2.	9.4	.0025	1.07	.342	.134	5.9	5.95
3.	9.4	.0025	1.08	.342	.344	5.85	5.95
4.	25.	.0025	1.04	.342	.150	7.6	7.6
5.	25.	.0025	1.16	.171	.100	7.45	7.6
6.	25.	.005	1.16	.342	.160	7.45	7.6
7.	25.	.005	1.07	.342	.037	7.55	7.6
8.	25.	.010	1.07	.342	.024	7.55	7.6
	50.	"	"	"	"	8.9	9.0
9.	40.	.0025	1.09	.342	.111	8.55	8.5
10.	50.	.0025	1.15	.171	.067	9.05	9.0
11.	50.	.005	1.07	.342	.049	8.9	9.0
12.	50.	.010	1.15	.342	.046	9.0	9.0
13.	50.	.0113	1.33	.171	.025	8.9	9.0

values of r_1 show little deviation from the values calculated by these equations. As before, the value of r_1 at a given pressure of filtration is found to be independent of concentration and of small variations of viscosity, and has the same value in the latter stages of a mixed pressure experiment, as it has in a single pressure experiment. Further, in Table V., some experiments were carried out using a filtering area of .342/2 = .171 sq.dm., instead of .342 sq.dm., and the specific resistance at a given pressure can be seen to remain unchanged, as demanded by equation (24).

It is difficult to account for the three different values of s in $r = r_1' P^s$ for ferric oxide, namely, .41, .18, and .25. As already noted, however, the distribution of particle sizes in the three stocks could not have been the same, and it is probable that the differences in the values of s are a direct result of these differences of particle size. As ferric oxide consists of rigid particles, it is to be expected that it should give an ideal cake, i.e., that s should be zero. On the other hand, the susceptibility of finely-ground ferric oxide to coagulation by electrolytes suggests that a considerable portion is in a state of division approaching that of colloidal particles. This colloidal material would always be coagulated to some extent into flocs and these flocs it is which would act as deformable particles in a cake. If this be true, the compressibility of a cake

should depend upon the percentage of finest, flocculated particles which are present, and each of the stocks A, B and C should, therefore, give a cake exhibiting a specific value of S.

It is interesting at this point to note that these Tables provide a certain amount of evidence for the assumption that the cloth resistance has the same compressibility as has the cake resistance. In many of the experiments, and particularly in Expt.9 in Table IV. and in Expt.5 in Table V., the cloth resistance has very high values, when it is remembered that the total volume of filtrate seldom exceeds .800 litre. Yet, in each case, the graph of θ/V' vs. V' is obtained as a straight line, and the resulting values of r_1 are not inaccurate. According to Appendix I., if cake and cloth compressibilities be very different, the errors for such high cloth resistance can be serious. Again, though high values of V_0 occur in many of the mixed pressure experiments, there prove to be no marked errors introduced by assuming that V_0 remains constant at the higher pressures.

Table VI. summarises the experiments with whiting. The cakes show a distinct compressibility, for r_1 varies according to $r_1 = 1{\cdot}09\, P'^{14} \times 10^6$. Comparison between experimental values of r_1 and values calculated from this formula is given in the last two columns of the Table. Not only have pressure, concentration and area been altered in this case, but,also, in experiments 5 and 6, a considerable alteration of

TABLE VI. Experiments with Whiting.

Expt.	P in lb./sq.in.	C in kg./litre	η in centi-poises	A in sq. dm.	V_0 in litres	r_c in $\frac{(sec.)^2}{kg.} \times 10^{-6}$	$1.09\,P^{1/4}$ (P in kg./sq.dm)
1.	9.4	.011	1.10	.342	.075	1.98	1.96
	25.	"	"	"	"	2.28	2.25
2.	9.4	.0121	1.07	.342	.043	1.97	1.96
	25.	"	"	"	"	2.24	2.25
	50.	"	"	"	"	2.44	2.48
3.	25.	.011	1.12	.171	.040	2.24	2.25
	50.	"	"	"	"	2.52	2.48
4.	25.	.0244	1.14	.342	.012	2.27	2.25
	50.	"	"	"	"	2.44	2.48
	100.	"	"	"	"	2.73	2.73
5.	25.	.0145	5.8	.342	.036	2.19	2.25
	50.	"	"	"	"	2.42	2.48
6.	25.	.0145	2.44	.342	.040	2.31	2.25
	50.	"	"	"	"	2.54	2.48
7.	50.	.011	1.14	.171	.025	2.42	2.48
	100.	"	"	"	"	2.75	2.73
8.	50.	.022	1.08	.342	.018	2.46	2.48
	100.	"	"	"	"	2.76	2.73

viscosity has been introduced. This was effected by replacing distilled water with a solution of the non-electrolyte, glycerol, in Expt.5, and by a solution of the electrolyte, calcium chloride, in Expt.6. In all cases, r_1 remains unchanged for any given value of P.

Kieselguhr is usually assumed to give an ideal cake. In Table VII., it will be seen that r_1 is constant from 4.7 lb./sq.in. to 25 lb./sq.in., but that, at 50 lb./sq.in., it has increased a little, while, at 100 lb./sq.in., there is a very decided increase. Apparently, at the lower pressures, the rigid particles of kieselguhr are able to withstand the unbalanced or deforming pressures within the cake, whereas, at the higher pressures, these deforming pressures become too great, and some of the particles are crushed. It should be remembered that kieselguhr particles are the skeletons of marine organisms and are, therefore, not solid, but porous and easy to crush.

No equation is suggested to fit the relation of r_1 to P, though it is nearly linear between 25 lb./sq.in. and 100 lb./sq.in. Table VII. also includes several variations of viscosity. In this instance, solutions of sucrose were used for the purpose. The agreement is good.

At first, sucrose solutions were also used with whiting and with ferric oxide to alter viscosity, but, in every case, the values of r_1 proved much too high, e.g.,

TABLE VII. Experiments with Kieselguhr.

Expt.	P in $\frac{\text{lb.}}{\text{sq.in.}}$	C in $\frac{\text{kg.}}{\text{litre}}$	η in centi-poises	A in sq.dm.	V_0 in litres	r_1 in $\frac{(\text{sec.})^2}{\text{kg.}} \times 10^{-6}$
1.	4.7	.018	1.06	.342	.004	1.17
	9.4	"	"	"	"	1.17
	14.1	"	"	"	"	1.17
2.	25.	.0073	1.04	.171	.040	1.15
	50.	"	"	"	"	1.21
3.	25.	.009	1.14	.342	.000	1.18
	50.	"	"	"	"	1.25
4.	25.	.018	1.04	.342	.019	1.15
	50.	"	"	"	"	1.24
5.	25.	.018	2.21	.342	.007	1.17
	50.	"	"	"	"	1.24
6.	25.	.018	2.53	.342	.000	1.15
	50.	"	"	"	"	1.23
7.	25.	.018	6.7	.342	.000	1.15
	50.	"	"	"	"	1.26
8.	100.	.018	1.08	.342	.236	1.34

with whiting, the following results are typical:

TABLE VIII. Experiments with Whiting Suspended in Solutions of Sucrose.
Area of filtering surface = .342 sq.dm.

P in lb./sq.in.	c in kg./litre	η in centipoises	$r_1 \times 10^{-6}$	r_1 at 100 lb./sq.in. / r_1 at 50 lb./sq.in.
50.	.011	2.6	3.01	1.07
100.	"	"	3.24	
50.	.022	2.67	2.75	1.09
100.	"	"	3.0	
50.	.011	6.7	3.23	1.05
100.	"	"	3.41	

According to $r_1 = 1.09 P^{.14} \times 10^6$, r_1 at 50 lb./sq.in. = 2.48×10^6
and r_1 at 100 lb./sq.in. 2.73×10^6

and ratio = 2.73/2.48 = 1.10

TABLE IX. Experiments with Ferric Oxide Suspended in Solutions of Sucrose.
Area of filtering surface = .342 sq.dm.

P in lb./sq.in.	c in kg./litre	η in centipoises	$r_1 \times 10^{-6}$	r_1 at 100 lb./sq.in. / r_1 at 50 lb./sq.in.
50.	.005	2.27	13.35	1.12
100.	"	"	15.2	
25.	.010	2.22	9.1	
50.	"	"	10.4	1.17
100.	"	"	12.2	
50.	.005	6.6	20.7	1.06
100.	"	"	22.0	

According to $r_1 = 2.08 P^{.25} \times 10^6$, r_1 at 25 lb./sq.in. = 7.6×10^6,
r_1 at 50 lb./sq.in. = 9.0×10^6,
and r_1 at 100 lb./sq.in. = 10.7×10^6

and ratio = 10.7/9.0 = 1.19.

It is not believed by the writer, however, that these results disprove equation (24), but rather that sugar has a peptising effect on the slurries, and causes, therefore, the formation of a more compact, highly-resistant cake. No alteration of r_1 was observed for kieselguhr cakes, in which the particles were too large for peptisation, and the effect was much smaller for whiting than it was for the more finely-divided ferric oxide. Moreover, not only have the values of r_1 for whiting and for ferric oxide been increased, but the compressibility of the cakes has also been altered, as evidenced by the ratios of $\frac{r_1 \text{ at } 100 \text{ lb./sq.in.}}{r_1 \text{ at } 50 \text{ lb./sq.in.}}$ shown in Tables VIII. & IX. These facts do provide some evidence for ascribing the anomalous behaviour of sucrose solutions to peptisation. Further, the results with glycerol and with calcium chloride solutions provide positive evidence in favour of equation (24).

In Table X., the results with a refined clay are given. The negative signs for P stand for vacuum filtrations in which the pressure of filtration was P. As discussed in the theoretical treatment, the value of r_1 for a given value of P, according to the theory of particle deformation, should be the same both in a vacuum filtration and in a positive pressure filtration. According to Underwood's theory, it should be greater in a positive pressure filtration. Since the absolute pressure, P_a, on the filtrate side of the cloth is 14.7 lb./sq.in.

TABLE X. Experiments with Clay.

Expt.	P in lb./sq.in.	c in kg./litre $\times 10^3$	η in centi-poises	A in sq.dm.	r_1 in $(\text{sec.})^2$/kg. $\times 10^{-6}$	$r_1 \times 10^{-6}$ (average values)
1.	-1.56	3.35	1.00	.342	1.92	1.92
	-3.12	"	"	"	2.40	2.40
2.	3.12	6.70	1.11	.342	2.38	2.40
	6.25	"	"	"	2.9	3.0
	12.5	"	"	"	3.7	3.75
	25.	"	"	"	4.75	4.85
3.	-3.12	6.70	1.12	.342	2.41	2.40
	-6.25	"	"	"	3.05	3.0
	-12.5	"	"	"	3.8	3.75
4.	12.5	13.4	1.14	.342	3.8	3.75
	25.	"	"	"	4.85	4.85
	50.	"	"	"	6.4	6.4
5.	25.	3.35	1.06	.171	4.85	4.85
	50.	"	"	"	6.4	6.4
6.	25.	13.4	1.12	.342	4.85	4.85
	50.	"	"	"	6.45	6.4
	100.	"	"	"	8.95	8.85
7.	25.	13.4	2.23	.342	5.0	4.85
	50.	"	"	"	6.3	6.4
8.	25.	13.4	6.5	.342	4.85	4.85
	50.	"	"	"	6.4	6.4
9.	50.	6.70	1.11	.171	6.45	6.4
	100.	"	"	"	8.85	8.85
10.	100.	26.8	1.25	.342	8.95	8.85
11.	100.	67.0	1.27	.342	8.65	8.85

for positive pressure filtration, and (14.7 - P) lb./sq.in. for a vacuum filtration, the difference, if any, will be most marked when P approaches 14.7 lb./sq.in.

The results in Table X. show no such difference, even when P = 12.5 lb./sq.in., i.e., when the values of P_2 are 14.7 lb./sq.in. and 2.2 lb./sq.in. for positive pressure and for vacuum filtration, respectively. r_1 is thus shown to be independent of concentration, area, viscosity, "single-pressure" or "mixed-pressure" method of filtration, and of the back pressure, P_2 . As regards variation with pressure of filtration, P , the compressibility is considerably greater than in the previous cases, except for Stock A of ferric oxide in Table II.

The plot of log. r_1 vs. log. P is not quite a straight line, as may be seen from Fig.16. The curvature is so slight, however, that a straight line may be drawn, as shown, which departs no more than 6% from the experimental points.

Viscosities were varied in Experiments 7 & 8 by using glycerol solutions. These two experiments demonstrate that the viscosity term in equation (24) is true even for such compressible cakes as those given by clay. It should be noted, however, that sucrose solutions gave rise to an increase in r_1 of more than 100%, probably due to peptisation.

In Table XI., there are set forth the results for

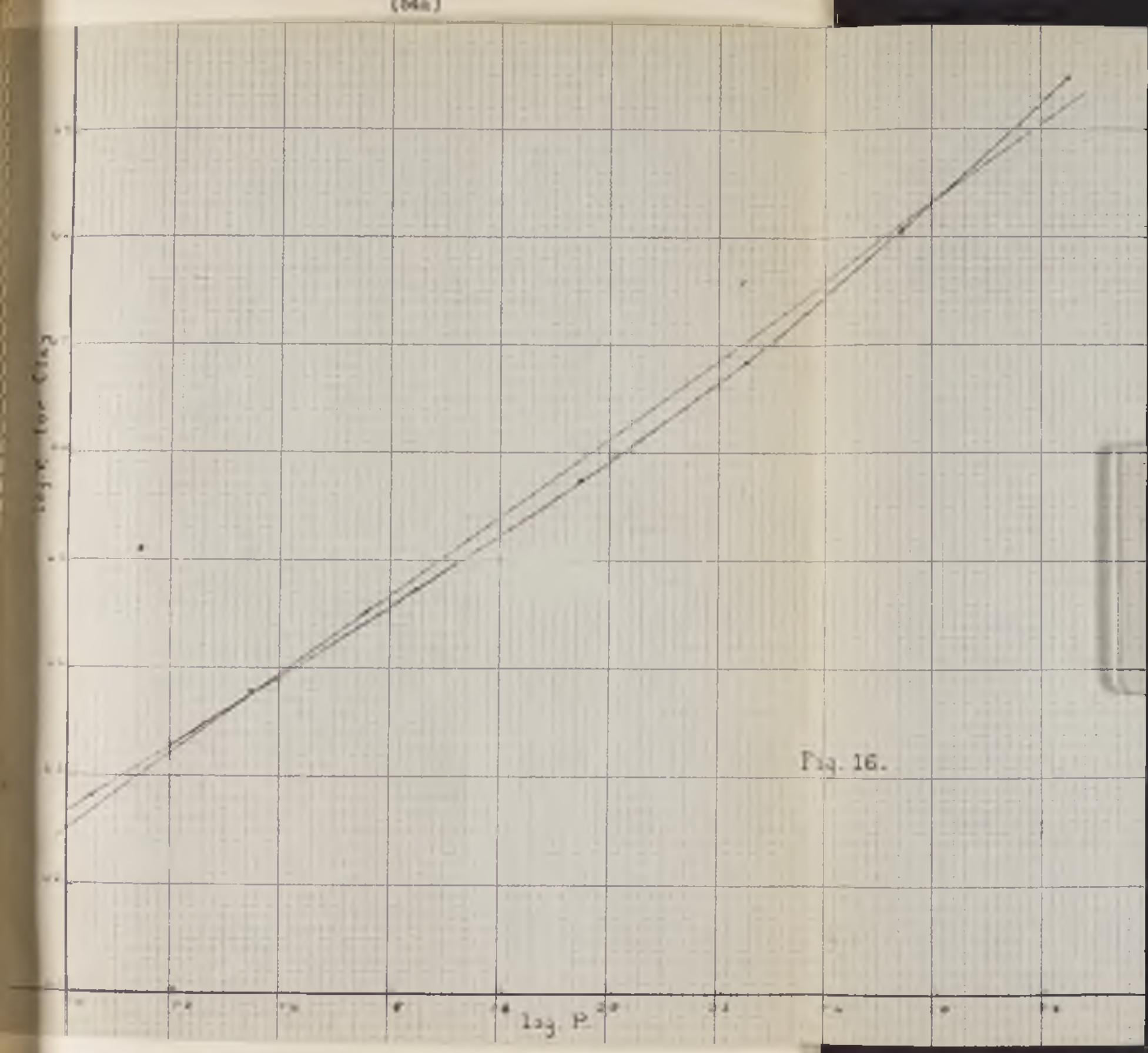


Fig. 16.

TABLE XI. Experiments with Magnesium Hydroxide.

Expt.	P in lb./sq.in.	C in kg./litre $\times 10^4$	η in centi-poises	A in sq.dm.	r_1 in $\frac{(sec.)^2}{kg.} \times 10^{-7}$	$r_1 \times 10^{-7}$ (average values)
1.	3.12	8.0	1.20	.342	1.33	1.33
	6.25	"	"	"	1.73	1.71
	12.5	"	"	"	2.3	2.33
2.	-3.12	8.0	1.11	.342	1.33	1.33
	-6.25	"	"	"	1.72	1.71
	-12.5	"	"	"	2.4	2.33
3.	6.25	8.0	1.29	.342	1.72	1.71
	12.5	"	"	"	2.35	2.33
4.	-6.25	8.0	1.25	.342	1.68	1.71
	-12.5	"	"	"	2.3	2.33
5.	12.5	8.0	1.24	.342	2.35	2.33
6.	-12.5	8.0	1.18	.342	2.3	2.33
7.	12.5	8.0	1.17	.342	2.3	2.33
	25.	"	"	"	3.2	3.35
8.	25.	8.0	1.12	.342	3.35	3.35
9.	25.	8.0	1.11	.342	3.35	3.35
	50.	"	"	"	4.8	4.85
10.	25.	16.0	1.31	.342	3.5	3.35
	50.	"	"	"	4.85	4.85
	100.	"	"	"	7.1	7.1
11.	50.	16.0	1.31	.342	4.85	4.85
	100.	"	"	"	7.1	7.1
12.	50.	8.0	1.29	.171	4.95	4.95
13.	100.	8.0	1.24	.171	7.15	7.1

magnesium hydroxide. The material for these experiments was drawn from a large stock of a thick magnesium hydroxide slurry obtained by adding milk of lime to a residue from Dead Sea water. The sample was washed free of its mother liquor, a strong solution, mainly, of calcium chloride, by a series of decantations with distilled water, first by gravity settling, and finally in a centrifuge. A thick slurry was thereby obtained of washed magnesium hydroxide in distilled water, and portions of this were diluted with distilled water for the experiments in Table XI.

The original slurry was being filtered in a 7-chamber laboratory filter press, of 63.7 sq.dm. area of filtering surface, under a gravity head of 17.5 feet of slurry, i.e., 8.3 lb./sq.in. pressure of filtration. It was, therefore, decided to compare the values of r_1 obtained with this large area of filtering surface with that obtained on the small filter of .342 sq.dm. area of filtering surface. A portion of the slurry was diluted with mother liquor, i.e., filtrate from the laboratory filter press, to 9% of its original concentration, and was used on the small filter at the same pressure and temperature of filtration. The significant data are as follows:

P $\frac{kg.}{sq.dm.}$	c $\frac{kg.}{litre}$	η centi-poises	A sq.dm.	b	$r_1 \times 10^{-7}$
58.5	.0587	1.28	63.9	5.54	3.5
58.5	.0053	1.28	.342	16.5 x 10	3.35

The agreement is very good, when it is considered that the ratio of the square of the areas is $63.9^2/.342^2 = 34,800$.

These two experiments stand apart from those in Table XI., which deals with the washed magnesium hydroxide, and for which the value of r_1 when $P = 8.3$ lb./sq.in. is much lower, namely, 1.92×10^7.

Magnesium hydroxide is a gelatinous material of indefinite degree of hydration and differs, therefore, quite sharply from the previously considered materials, which are rigid in the massive form. Yet, as before, the specific resistance, r_1, is dependent upon the pressure of filtration, P, alone, and the plot of log. r_1 vs. log. P shows but little deviation from linearity, as shown in Fig.17. The straight line which has been drawn in the figure would not give an error of more than 6% in r_1, in the range of pressures used.

The same generalisations apply to the aluminium hydroxide and ferric hydroxide slurries, summarised in Tables XII. & XIII., respectively, with the exception that the curvatures of the log. r_1 vs. log. P plots, though also convex to the log. P -axis, are more marked, so that the straight lines drawn in Figs.18 & 19 deviate to a greater extent from the experimental points. The maximum error for the given range of pressures is 7% for the aluminium hydroxide curve, and 12% for the ferric hydroxide curve.

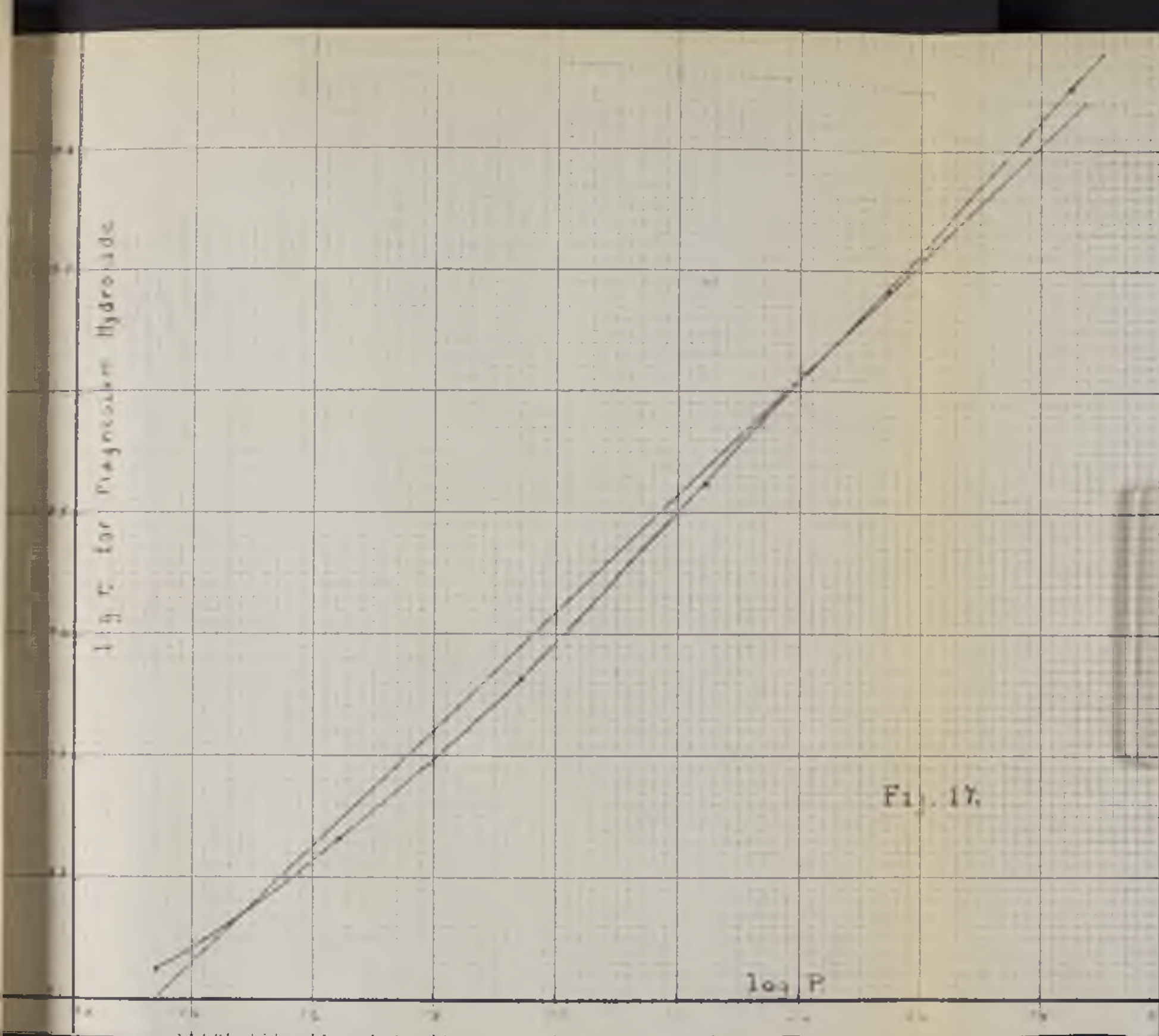


Fig. 17.

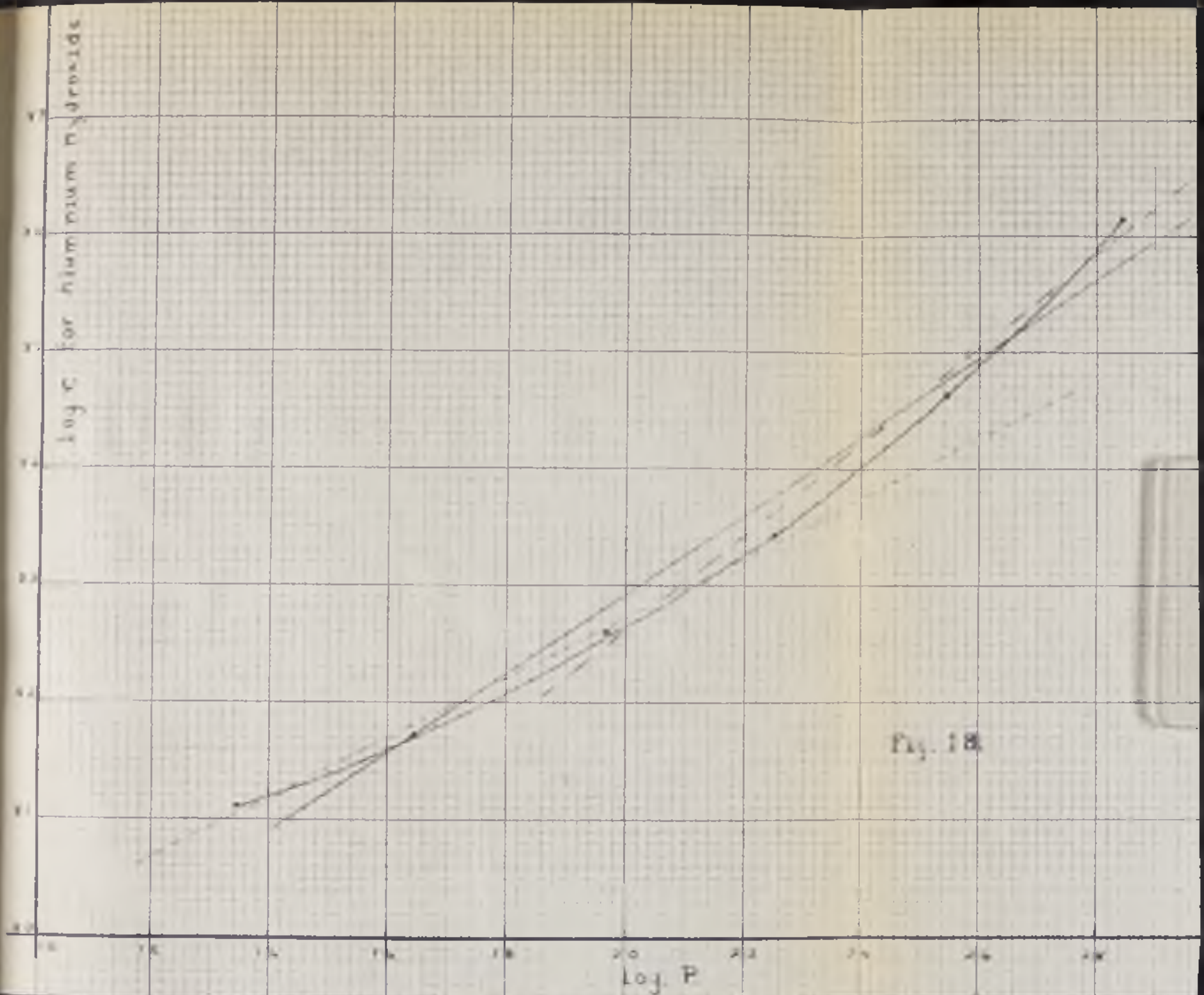


Fig. 18

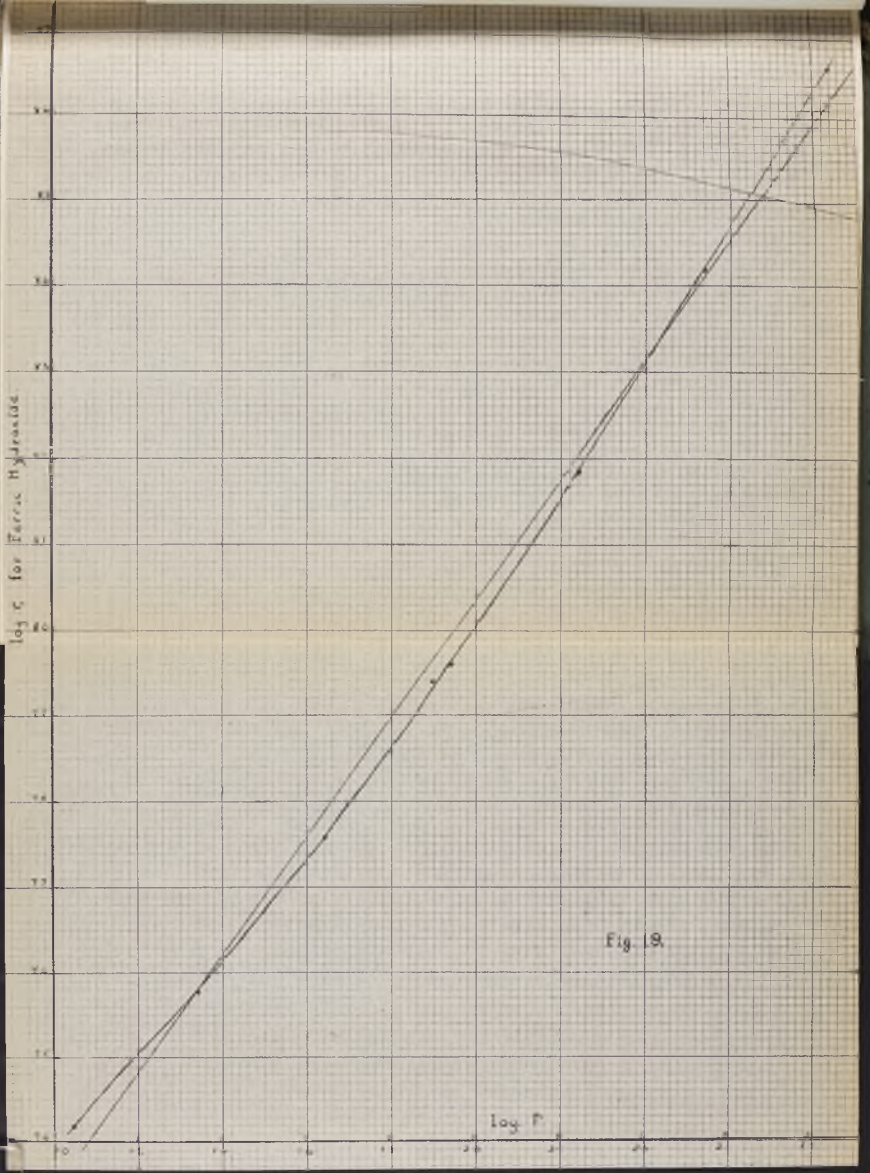


Fig. 19.

TABLE XII. Experiments with Aluminium Hydroxide.

Expt.	P in lb./sq.in.	c in kg./litre $\times 10^4$	η in centi-poises	A in sq.dm.	r_1 in $(sec.)^2/kg. \times 10^{-8}$	$r_1 \times 10^{-8}$ (average values)
1.	-3.15	5.7	1.24	.342	1.29	1.29
	-6.25	"	"	"	1.46	1.49
	-12.5	"	"	"	1.81	1.82
2.	-6.25	2.85	1.35	.342	1.53	1.49
	-12.5	"	"	"	1.87	1.82
3.	-6.25	5.7	1.24	.342	1.49	1.49
	-12.5	"	"	"	1.81	1.82
4.	12.5	5.7	1.33	.342	1.81	1.82
	25.	"	"	"	2.22	2.20
	50.	"	"	"	2.94	2.91
	100.	"	"	"	4.2	4.15
5.	12.5	5.7	1.29	.342	1.81	1.82
	25.	"	"	"	2.15	2.20
	50.	"	"	"	2.85	2.9
6.	-12.5	5.7	1.35	.342	1.83	1.82
7.	25.	5.7	1.35	.342	2.22	2.20
	50.	"	"	"	2.88	2.9
	100.	"	"	"	4.05	4.15
8.	50.	11.4	1.35	.342	2.98	2.9
	100.	"	"	"	4.1	4.15
9.	50.	5.7	1.29	.171	2.92	2.9
10.	100.	11.4	1.31	.171	4.1	4.15
11.	100.	28.5	1.31	.342	4.2	4.15

TABLE XIII. Experiments with Ferric Hydroxide.

Expt.	P in lb./sq.in.	C in kg./litre $\times 10^4$	η in centi-poises	A in sq.dm.	r_1 in $(sec.)^2$/kg. $\times 10^{-7}$	$r_1 \times 10^{-7}$ (average values)
1.	-1.56	3.7	1.20	.342	2.62	2.62
	-3.12	"	"	"	3.8	3.8
	-6.25	"	"	"	5.85	5.7
2.	-3.12	4.6	1.22	.342	3.75	3.8
	-6.25	"	"	"	5.7	5.7
	-12.5	"	"	"	9.1	9.1
3.	6.25	4.6	1.24	.342	5.6	5.7
	12.5	"	"	"	9.05	9.1
	25.	"	"	"	15.0	15.2
4.	-11.3	9.2	1.20	.342	8.6	8.7
5.	11.3	9.2	1.27	.342	8.75	8.7
	25.	"	"	"	15.2	15.2
	50.	"	"	"	25.2	26.
6.	25.	9.2	1.24	.342	15.4	15.2
7.	25.	9.2	1.20	.342	15.3	15.2
8.	25.	3.1	1.20	.171	15.2	15.2
9.	50.	9.2	1.22	.171	26.1	26.
10.	50.	4.6	1.20	.342	26.5	26.
	100.	"	"	"	45.0	45.5
11.	100.	9.2	1.27	.342	46.0	45.5

Discussion of the Relationship between r_1 and P.

It has been sufficiently established, in the presentation of the results, that equation (24) has a wide enough generality to cover the filtration of all types of materials, varying from those giving nearly ideal cakes, such as kieselguhr, to those giving extremely compressible cakes, such as ferric hydroxide. As required by this equation, r_1 depends upon P alone, where P is the pressure of filtration, i.e., the pressure difference across cake and cloth.

The nature of the function relating r_1 and P does not appear, however, to be as simple as is generally assumed. Leaving out of account kieselguhr, which probably departs from ideality at high pressures owing to a collapse of some of its porous particles, we find there is little departure from $r_1 = r_1' P^s$ for whiting or for ferric oxide, i.e., log. r_1 vs. log. P is a straight line, the gradient of which is s. In the case of clay, however, there is a decided curvature in log. r_1 vs. log. P, convex to the log. P-axis. This could be expressed by saying that s is a variable, increasing when P increases. The same applies to the three metallic hydroxides, the curvature being, in all cases, in the same sense. It shows up particularly for aluminium hydroxide and for ferric hydroxide.

It is possible that this curvature has become noticeable owing to the use of a wider range of pressures for

these four materials. In a range of 9.4 lb./sq.in. to 100 lb./sq.in., which was used in Tables II., IV., & VI., they also give a very close approximation to linearity in log. r_1 vs. log. P plots. Again, it is not to be expected that a slight curvature would show where s is not very large, for the changes in r_1 between successive values of P are not then very great, and departures from true linearity would tend to be masked by the experimental errors in in the determination of r_1.

The evidence appears to suggest that a like curvature is characteristic of all plots of log. r_1 vs. log. P, and, indeed, this is to be expected. According to the equation, $r_1 = r_1' P^s$, if the pressure of filtration be steadily reduced, r_1 will decrease to a limiting value of zero, i.e., $\lim_{P \to 0} (r_1) = 0$. The resistance of a cake can only be zero when the distance between the particles is infinite, or, in practical terms, when the particles remain suspended in the slurry and there is no cake at all. It is a little difficult to picture a process of filtration in which the pressure of filtration is zero, but an approach can be made to the problem by considering the definition of r_1, according to the theory of particle deformation, as $1/r_1 = 1/P \int_0^P dP/r$ where r is the specific resistance at any point in the cake, so that, when $r = r' P^s$, $r_1 = r_1' P^s$ where $r_1' = (1-s) r'$. At the surface of the cake, $P = 0$, and, when the pressure of filtration is zero, the

condition at the surface of the cake is uniform throughout the cake, i.e., $r_{p=0} = \mathcal{L}t_{p\to 0}(r_1)$. If $r = r' p^s$, then, when $p = 0$, $r = 0$, which, expressed in physical terms, means that the surface of the cake merges with the slurry with no sharply-defined boundary between the two. Now, even for an extremely compressible cake such as that given by ferric hydroxide, though the surface layers of the cake are very soft and wet compared with the layers next to the cloth, there is still a distinct boundary between cake and slurry. The value of r at the surface of the cake, and the value of $\mathcal{L}t_{p\to 0}(r_1)$, should, therefore, be a definite positive quantity, the specific resistance of the undeformed particles packed in the surface of the cake.

Thus the meaning of the curvature obtained in the log. r_1 vs. log. P plots is that the values r_1 at low values of P tend to approach a positive limiting value instead of a value of zero. In this connection, the experiments of Gilse, Ginneken and Waterman[8] are of interest, for they establish the relation $r_1 = r''(1 + \alpha P)$, so that $\mathcal{L}t_{p\to 0}(r_1) = r''$. The actual values of r_1 for the activated carbons which they used are

Norit	: $r_1 = .618(1 + .0302\ P) \times 10^5$
Eponit	: $r_1 = .655(1 + .0252\ P) \times 10^5$
Nobrac	: $r_1 = 1.720(1 + .0205\ P) \times 10^5$
Carboraffin	: $r_1 = 2.90\ (1 + .0151\ P) \times 10^5$

where P is in kg./sq.dm., and their pressures did not exceed 10 lb./sq.in., i.e., P did not exceed 70 kg./sq.dm.

These carbons were, therefore, even more easily filtrable than the kieselguhr used for Table VII. Apparently, they furnish an extreme case of the curvature observed in log. r_1 vs. log. P plots, and suggest that the relation between r_1 and P always becomes linear when P approaches zero.

Apart from kieselguhr, however, none of the present materials showed a similar behaviour. Though the curvature of log. r_1 vs. log. P plots did tend to show that $\lim_{P \to 0}(r_1)$ is nor zero, this curvature was not very marked, and, even for low values of P, the plot of r_1 vs. P showed no tendency to approach linearity.

It would be of interest to find if the values of r_1 for the activated carbons fell below those predicted by the linear equations at higher values of P, and an attempt was made to test this with Carboraffin. The rate of flow, however, proved too great for the capacity of the present apparatus, and the attempt had to be abandoned.

In making practical use of equation (24), the most important point to be observed is that the simple equation, $r_1 = r_1' P^s$ can be used over wide ranges of pressure without admitting an error of more than 5% - 10% in r_1. In this matter, the value of s, which is the gradient of the log. r_1 vs. log. P plot, should be governed by the range of pressures within which it is proposed to work. For example, if a slurry of aluminium hydroxide were being filtered, we should use the equation

$r_1 = \cdot 42 P^{\cdot 34} \times 10^8$ for the range 3.1 lb./sq.in. to 100 lb./sq.in., but, for the range 3.1 lb./sq.in. to 12.5 lb. /sq.in., a much closer approximation is given by $r_1 = \cdot 58 P^{\cdot 26} \times 10^8$, and, for the range, 12.5 lb./sq.in. to 100 lb./sq.in., by $r_1 = \cdot 27 P^{\cdot 41} \times 10^8$, and similarly for other limited ranges. The values of s for such ranges are given below for clay and for the three metallic hydroxides.

Material	1.56 lb./sq.in. to 100 lb./sq.in.	1.56 lb./sq.in. to 12.5 lb./sq.in.	12.5 lb./sq.in. to 100 lb./sq.in.
clay	.37	.32	.42
magnesium hydroxide	.47	.42	.53
aluminium hydroxide	.34	.26	.41
ferric hydroxide	.69	.59	.76

In industrial practice, the range most commonly used is 10 lb./sq.in. to 100 lb./sq.in., and, within this, the equation, $r_1 = r_1' P^s$, holds almost within the limits of experimental error. Thus, the particular form of equation (24)

$$dV/d\theta = P^{1-s} A^2 / \eta r_1' c (V + V_0) . \qquad (24a$$

has sufficient generality for all industrial purposes.

Theoretical Discussion of Constant Rate Filtrations.

Many filtration processes in industry are not carried out at constant pressure. The initial pressure is small and, as the cake builds up, the pressure is steadily increased to keep the rate of flow approximately constant. Baker[15] has claimed that this method yields a greater volume of filtrate within a given time than does the constant pressure method of working, but this generalisation is open to criticism.

It has been shown that the specific resistance, r_1, for a given value of P has the same value in a single pressure filtration as it has in a mixed pressure filtration, so that equation (24) is applicable to both. It applies, therefore, to constant rate filtration as well, for this is really a mixed pressure filtration with an infinite number of constant pressure stages, each maintained for an infinitesimal instant of time. Therefore, using equation (24a)

$$\text{i.e.,} \quad dV/d\theta = V/\theta = P^{1-s} \cdot A^2 / \eta r_1' c (V+V_0) = k_1$$

where the rate of flow is a constant, k_1, and P is a variable, the relation between the volume filtered in a given time, θ, and the final pressure of filtration, P_f, is given by

$$(P_f)^{1-s} = \eta r_1' c V (V+V_0) / \theta . A^2 .$$

If we filter the same volume in the same time at a constant pressure, P_c, we have

$$P_c^{1-s} = \eta r_1' c V (V+2V_0) / 2\theta A^2 .$$

whence

$$\left(P_f/P_c\right)^{1-s} = 2 . (V+V_0) / (V+2V_0) .$$

We may neglect cloth resistance, as it does not affect the general argument, so that

$$P_b/P_c = 2^{1/1-s}$$

For an ideal cake, where $s = 0$, $P_b/P_c = 2.0$

For whiting, where $s = .14$, $P_b/P_c = 2.25$

For magnesium hydroxide, where $s = .47$, $P_b/P_c = 3.7$

For ferric hydroxide, where $s = .69$, $P_b/P_c = 9.35$.

These are conservative values of P_b/P_c, when it is remembered that s increases when the pressure is increased, e.g., for ferric hydroxide, the value of s in the range, 12.5 lb./sq.in. to 100 lb./sq.in. is not .69, but .78. Thus, for constant rate filtration to exceed constant pressure filtration in efficiency, the final pressure must be more than twice that in a constant pressure filtration, for an ideal cake, and more than 9.35 times for a cake of ferric hydroxide. It is possible to obtain a greater efficiency, therefore, and it is practicable to do so, as long as s does not exceed .5. But, with more compressible cakes, the final pressures required are of such a magnitude that a much stronger and more expensive filter would be required, and the extra cost would more than offset the advantages of an increased capacity.

Another use of constant rate methods has been for the laboratory determination of filtration constants. If we neglect cloth resistance, equation (24a) becomes, for constant rate conditions,

$$V = P^{1-s} \cdot A^2/\eta r_1' c k_1$$

so that, plotting log. V vs. log. P, we should get a straight line, the gradient of which is $(1-s)$, and then, from any given pair of values of V and of P, and a knowledge of the values of A, η, c, k_1, s, r_1' can be calculated. This method has been used by Donald and Hunneman,[11] and by Weber and Hershey,[12] both of whom modified it by introducing a correction for cloth resistance. They extrapolated the plot of V vs. P to $V=0$, cutting the P-axis at P_o, and then plotted log. V vs. log. $(P-P_o)$, instead of log. V vs. log. P. This correction is true if the cloth resistance remains constant, i.e., if the cloth is an ideal filter medium.

If, however, the cloth resistance and the cake resistance show approximately the same degree of compressibility a different correction should be used, for them the term, V_o, in equation (24a),

$$dV/d\theta = k_1 = P^{1-s} A^2 / \eta r_1' c (V+V_o)$$

is independent of the value of P. This equation gives

$$(V+V_o) = P^{1-s} A^2 / \eta r_1' c k_1$$

whereas the introduction of P_o leads to the equation,

$$V = (P-P_o)^{1-s} A^2 / \eta r_1' c k_1$$

If V_o is a constant, the proper way to allow for cloth resistance is to plot V vs. P, and to extrapolate to $P=0$ cutting the V-axis at $-V_o$. Then, plotting log. $(V+V_o)$ vs. log. P should yield the required result.

Unfortunately, the plot of V vs. P tends to approach the V-axis at a very acute angle, so that it is

difficult to estimate the value of V_o with any degree of accuracy. This could be overcome by modifying the experimental method slightly. If we carry out the first part of the experiment at constant pressure, the plot of θ/v' vs. V' will give the value of V_o, together the value of r_1 at the given pressure. The remainder of the experiment can then be carried out at constant rate, and $\log.(V+V_o)$ be plotted against $\log. P$

The Relation between Small-scale and Large-scale Experiments.

The main difference lies in the difference of the area of the filtering surfaces. In making calculations for a large-scale filter from experiments on a small-scale filter, the ratio of the square of the areas must be used. This is a very large term, e. g., in the experiments cited on p.55, the ratio of the square of the areas was 34,800, and even then the area for the larger filter was only 63.9 sq.dm., representing a small laboratory filter press. In this particular case, the two values of r_1 were fairly closely in agreement, but, for safety, it is advisable to carry out an experimental run on the full-size filter or on a filter of intermediate size to ensure that results given by the small filter do not lead to too serious an error when applied to the larger filter.

Usually. too, the slurry used on the small filter is diluted considerably, since the original slurry would take too long to yield an appreciable amount of filtrate. There should not be much error from this source, however, provided

(i) that a sample be drawn from the slurry actually being filtered on the large scale, and (ii) that this sample be diluted with filtrate from the main slurry. These two points are of extreme practical importance.

The filtering properties of a slurry, as pointed out by Walker, Lewis and McAdams,[16] can easily show a fourfold variation for slight alterations in the method of preparation. It is useless to prepare a slurry in the laboratory and to predict from its properties the rate of filtration of a similar slurry prepared under works conditions. Again, the nature of the liquid in which the solid matter is suspended has usually a marked influence on the filtering properties of the slurry. The writer believes that the "deformable particles" which give rise to compressibility in the cake are flocs, except, perhaps, for a few cases such as the activated carbons of Gilse, Ginneken and Waterman, for which their explanation of an adsorbed film of water on the carbon particles is sufficient The state of aggregation of flocculated matter is very dependent upon the chemical nature of the liquid in which it is suspended, and, in this fact, it is believed, lies the reason for any change in the filtering properties when the nature of the liquid is altered.

Evidence is provided by the enhanced values of r, which result when distilled water is replaced by solutions of sucrose, for suspensions of ferric oxide, of whiting, and of

clay. This has already been discussed on p.53.

Further, some experiments with ferric hydroxide showed that suspensions in dilute calcium chloride solutions were more quick-settling than those in distilled water, and gave values of r_1 lower by 10% - 20%. On the other hand, dilute solutions of ferric chloride, which, though an electrolyte, contains an ion in common with ferric hydroxide, had so strong a peptising effect that very little ferric hydroxide settled from the slurries in 24 hours; and these slurries, when filtered, gave values of r_1 higher than normal by 50% and more. This is analogous with the known peptisation of silver chloride in the presence of dilute solutions of silver nitrate or of hydrochloric acid, both of which contain an ion in common with silver chloride.

It might be noted that, of the three hydroxides in Tables XI., XII., & XIII., the suspensions of aluminium hydroxide were much the most slow-settling, i.e., the most nearly colloidal, or least flocculated. They show a very high specific resistance and low compressibility compared with the other two hydroxides, and, to correspond, the cakes were thin, gelatinous films, showing little signs of "slushiness" at the surface, This fits with the more col oidal nature of aluminium hydroxide slurries, for, as the cake from a colloidal sol would consist of colloidal particles instead of flocs, it wouls be nearly impermeable, and would, moreover, show little

compressibility, as colloidal particles would be more difficult to deform than flocs.

So far, in this discussion of the correlation of small-scale and of large-scale filtrations, it has been assumed that equation (24) can be used for correlation, provided that the nature of the slurry remains unchanged. There is one other limitation to the use of this equation, which is of sufficient importance to rquire a section to itself.

Settling Effects.

Equation (24) is true only if (i) every equal volume of filtrate results in the deposition of an equal amount of cake, (ii) and if this cake be deposited evenly. By efficient stirring in the slurry-containing vessel, it is possible to ensure that a slurry delivered to the filter does not vary in concentration, and thus to fix the first of these conditions, but it is impossible to prevent a quick-settling slurry giving an uneven cake in the filter. In the filter press, the slurry must take a certain time from the moment it enters the press chamber to the moment it reaches the cake, for there must be a chamber of appreciable volume to hold the cake. In this time, the particles in the slurry have a chance to settle out, and this leads to an uneven cake.

Now, for a given amount of cake distributed over a given area, it is easy to prove that the evenly-distributed

cake is the cake of maximum resistance. Thus, the values of r_1 calculated from the time-volume readings for an uneven cake will tend to fall below their real value. To a certain extent, the cake will be self-healing, for the rate of flow will be greater at the thinner parts, so that the cake solids will be deposited more quickly at these parts, but this effect cannot be enough to correct the abnormally low values of r_1 .

Attention was called to these facts by some experiments with whiting slurries which were being filtered in a two-chambered , laboratory filter press, of 18.2 sq.dm. area of filtering suraface. The plots of θ/V' vs. V' , which should have yielded straight lines according to

$$\theta/V = bV' + a \qquad \text{where} \qquad b = \eta r_1 c/2PA^2 ,$$

though fairly straight for a considerable part of the experiment, were not straight for the whole of it. The gradients of the straight portions, b , were not proportional to the concentration, c , and the values of r_1 were much less than those obtained on the small filter of .342 sq.dm. of filtering surface. As these slurries were found to settle at the fast rate of 4" in 10 minutes, it seemed likely that these anomalous results were due to uneven deposition of the cake, and this was borne out by the appearance of the cakes.

Fig.20 shows the two cakes in a press chamber after filtration had progressed for three hours, So much solid matter had settled out in the bottom of the press chamber that

Fig. 20.

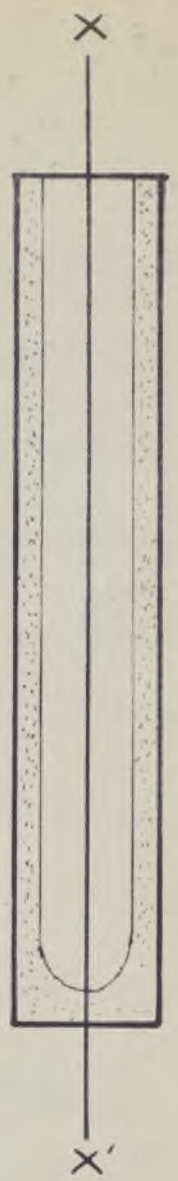


Fig. 21 b.

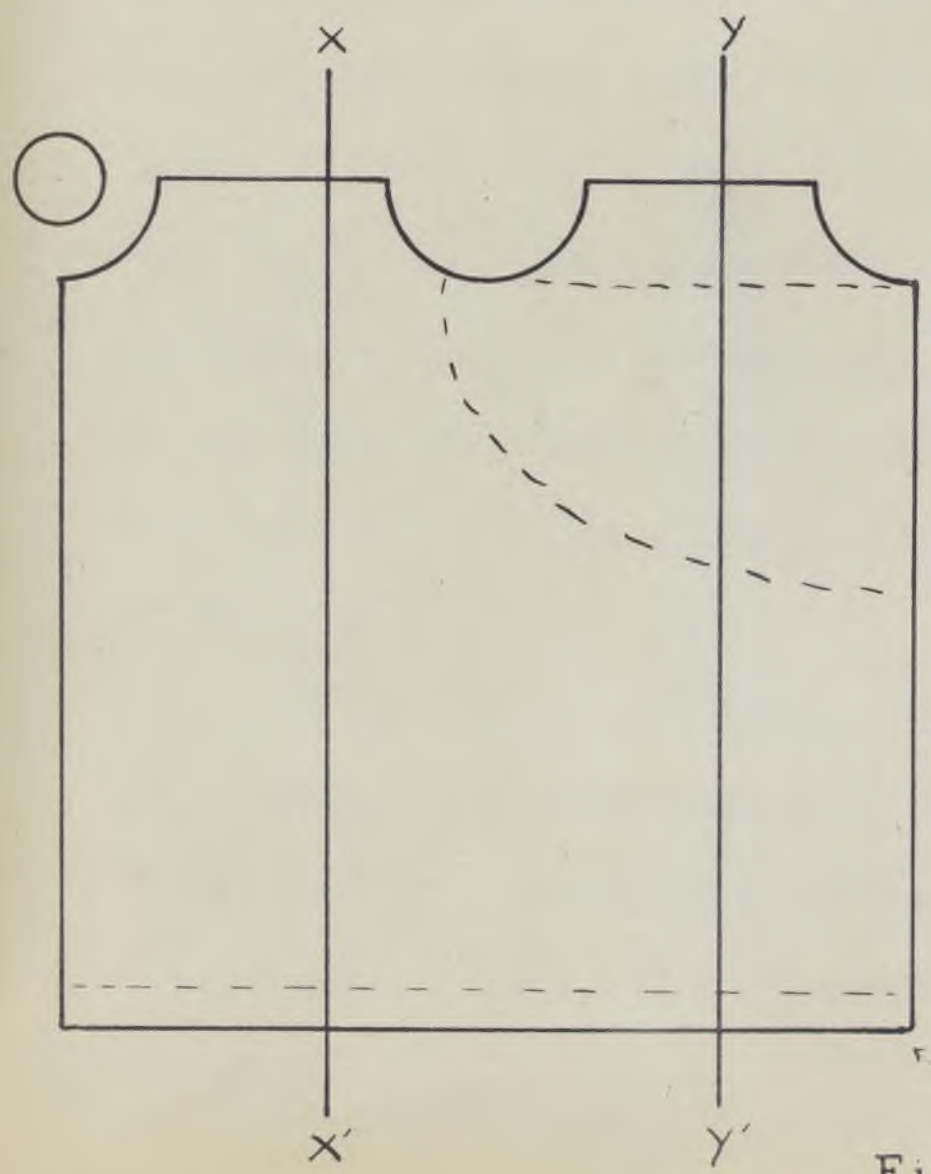


Fig. 21a.

the lower halves of the two cakes were fused together, leaving only half of the original surface free for filtering. The upper halves were very evenly-deposited, but this was probably due to the self-healing effects aforementioned. In Fig.21, a similar diagram is shown, when the press was opened after a single hour of filtering. In Fig.21a, there is shown a surface view of one of the cakes, indicating the position of the slurry delivery port, and the main areas of importance on the cake, and the lines XX' & YY' indicate the sectional views shown in Fig.21b. In the shorter time of filtration, there was a comparatively small amount of solids deposited at the bottom of the chamber, fusing the cakes together; and, in the upper parts of the cake most remote from the slurry port, the self-healing effects were insufficient to maintain an even cake thickness. This was particularly marked in the upper right hand corner of Fig.21a, as shown in the YY' section of Fig.21b, for there the cake thickness fell off sharply, indicating that, by the time the slurry had travelled to this corner, solids had settled out so completely that only clear liquid was left to filter.

In Table XIV., there are set forth the time - volume readings for the three hour filtration, and, from these, "b" = $\Delta(\theta/V')/\Delta V'$ is calculated for each stage in the experiment. If there were no settling, $\theta/V' = bV' + a$

i.e., $\Delta(\theta/V')/\Delta V' = b$ = constant.

TABLE XIV. Experiment Indicating the Settling of Whiting in a Laboratory Filter Press

Area of filtering surface = 18.2 sq.dm.
Concentration of Slurry = .075 kg./litre.
Viscosity of Filtrate = 1.16 centipoises.
Pressure of Filtration = 8.0 lb./sq.in.

θ in secs. x 10^{-2}	V' in litres	$\Delta V'$	θ/V'	$\Delta\theta/V'$	$\Delta(\theta/V')/\Delta V' = "b"$	$"r" \times 10^{-6} = "b" \times .433$
1.2	2.77		43.4			
2.4	4.80	2.03	50.0	6.6	3.25	1.41
4.8	7.95	3.18	60.4	10.4	3.30	1.43
8.4	11.71	3.76	71.6	11.2	2.98	1.29
12.0	14.86	3.15	80.8	9.2	2.9	1.26
19.2	20.21	5.35	95.0	14.2	2.65	1.15
24.0	23.3	3.09	103.1	8.1	2.62	1.13
28.8	26.12	2.82	110.2	7.1	2.52	1.05
38.4	31.23	5.11	122.9	12.7	2.49	1.04
44.4	34.11	2.88	130.1	7.2	2.50	1.04
56.4	39.3	5.19	143.4	13.3	2.56	1.11
68.4	43.9	4.6	155.8	12.4	2.69	1.17
80.4	48.0	4.1	167.4	11.6	2.83	1.23
98.4	53.47	5.47	184.1	16.7	3.05	1.32
110.4	56.63	3.16	195.0	10.9	3.45	1.50

and $r_1 = 2bPA^2/\eta c$

In the present case, $\Delta(\theta/V')/\Delta V'$, and the values of "r_1" calculated from it have no real meaning, but they show what is happening in the press chamber. At first, "r_1" decreases rapidly, indicating that the cake is depositing unevenly, and giving a lower resistance than would an evenly deposited cake. Then "r_1" settles to a fairly steady value for the greater part of the filtration, indicating that the tendency to settle to an uneven cake is being opposed by the tendency of the cake to heal itself. Meanwhile, the solids at the bottom of the chamber build up, gradually fusing the cakes together, and thereby decreasing the effective filtering surface, until this effect takes precedence over all others, and "r_1" begins to increase rapidly.

Part of the same slurry was then taken for the small filter of .342 sq.dm., the results being given in Table XV. for a horizontal filtering surface, and in Table XVI. for a vertical filtering surface. The shape of the cake in each case is indicated by the sectional views in Fig.22. The values of "r_1" correspond. For the horizontal cake, there was not the same opportunity for the cake to settle unevenly, and all solids had to settle on the cake itself. The values of "r_1", therefore, tend to be somewhat higher than in Table XIV. for the same time of filtration. On the other hand, where we have a vertical cake, as in the filter press, the ratio of the

Fig. 22.

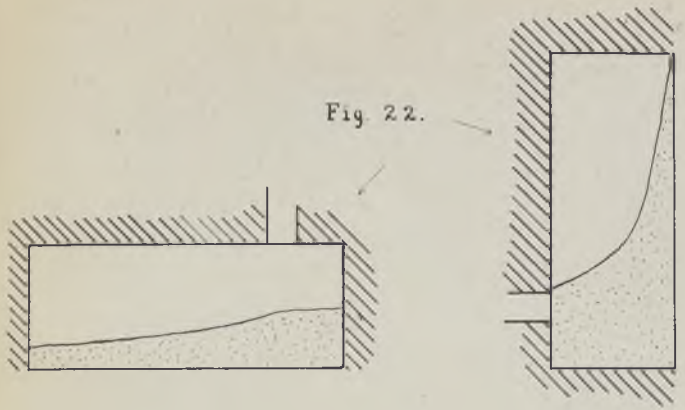


Fig. 23.

TABLE XV. Segregation of Whiting in a Small Filter.
Horizontal Filtering Surface.

Area = .342 sq.dm. Pressure = 8.0 lb./sq.in.
Concentration = .075 kg./litre. Viscosity = 1.17 centipoise.

θ in secs.	V' in litres	"r" x 10^{-6}
120	.048	
300	.099	1.51
540	.152	1.54
840	.207	1.40
1200	.263	1.35
1620	.321	1.28
2100	.379	1.31
2700	.444	1.28

TABLE XVI. Segregation of Whiting in a Small Filter.
Vertical Filtering Surface.

Area = .342 sq.dm. Pressure = 8.0 lb./sq.in.
Concentration = .063 kg./litre. Viscosity = 1.17 centipoises.

θ in secs.	V' in litres	"r" x 10^{-6}
120	.079	
240	.130	1.15
360	.172	1.07
540	.227	.93
720	.276	.84
960	.337	.71
1200	.392	.68
1500	.455	.68
1800	.513	.65
2100	.569	.58
2400	.621	.62
2700	.671	.54

chamber volume to the area of the filtering surface was much higher than for the filter press, and the slurry port was near the bottom of the chamber, both of which effects should exaggerate the settling effects observed in the filter press. This is well shown in the shape of the cake and in the low values of "r_1".

The experiments reported in Tables XVII. & XVIII., were experiments with a much diluted slurry, using a horizontal and a vertical filtering surface, respectively. The rates of flow were very much greater on this account, so that there was was less chance for settling to be effective. Correspondingly, the values of "r_1" are much higher than they are for the experiments in Table XV. & XVI. The cake on the horizontal surface was very nearly of an even thickness, while, on the vertical surface, the unevenness was fairly marked, see Fig.23.

These experiments show quite clearly that equation (24) is useless for quick-settling cakes. At the utmost, in equation (24), which is the specific resistance for an evenly deposited cake, gives the maximum specific resistance for the cake, so that the capacity of a filter press designed on this value would err on the safe side.

Yet, even this error would not be too marked if we filled the chambers in the filter press, for the blockage of the filtering surface, as revealed in Fig.20 and in Table XIV., decreases the average rate of flow for a full cycle very considerably.

TABLE XVII. Segregation of Whiting in a Small Filter.
Horizontal Filtering Surface.

Area = .342 sq.dm. Pressure = 8.0 lb./sq.in.
Concentration = .0105 kg./litre. Viscosity = 1.14 centipoises.

θ in secs.	V' in litres	"r" x 10^{-6}
60	.072	
120	.130	1.73
210	.202	1.77
300	.264	1.71
420	.339	1.51
540	.405	1.53
660	.467	1.45
780	.524	1.46
960	.603	1.42
1140	.677	1.40
1320	.746	1.35

TABLE XVIII. Segregation of Whiting in a Small Filter.
Vertical Filtering Surface.

Area = .342 sq.dm. Pressure = 8.0 lb./sq.in.
Concentration = .0105 kg./litre. Viscosity = 1.20 centipoises.

θ in secs.	V' in litres	"r" x 10^{-6}
60	.082	
120	.145	1.59
210	.224	1.45
300	.292	1.38
390	.353	1.31
510	.425	1.38
630	.493	1.20
780	.570	1.22
930	.643	1.09
1110	.724	.92
1260	.789	1.22

There is no point in modifying the slurry to make it less quick-settling, for, apart from ease of filtration being usually connected with quickness of settling, the uneven cake is a cake of lower resistance than the even cake, and is, therefore, desirable. Probably the best method of all for dealing with the matter is to take advantage of the quick-settling properties of the slurry by using a thickener before filtration. A thickened slurry is always better for filtering, as a greater amount of cake can be deposited in a given time. This is shown by equation (24), integrating, and leaving out the cloth resistance term,

$$\theta = \eta r_1 c V^2 / 2 P A^2 = \eta r_1 w^2 / 2 P e$$

where $w = cV/A$ = weight of cake per unit area. For a given value of w, the time of filtration, θ, is inversely proportional to the concentration, c. Moreover, the hindered rate of settling of the thickened slurry will tend to interfere less with the evenness of deposition of the cake, i.e., the deviation from equation (24) will tend to be less serious.

The Deformation of Paraffin Wax Particles.

An attempt was made to obtain visual evidence for the distribution of particle deformation in a filter-cake. A 125°F paraffin wax was melted and sprayed from a rapidly revolving spray-disc to give spherical particles of fairly uniform size, about .05 mm. diameter. These were suspended in a soap solution and filtered at 150 lb./sq.in. pressure. It

was necessary to keep the temperature at 30°C, as the wax was too hard to deform below this temperature. When the cake had been formed, small portions were taken from various sections and dispersed in drops of a strong soap solution upon microscope slides. Examination under the microscope showed that the particles from near the surface of the cake were still perfectly spherical in shape, but that those from near the cloth were distorted into polyhedra. This provided the necessary evidence, so that attention was concentrated upon obtaining photographs of the deformed particles.

Unfortunately, no success was obtained in showing the results in a striking manner. If a mass of spheres, tightly packed together, be compressed, a very slight flattening at the points of contact is sufficient to cause a very large decrease of the pore-space between the spheres. If, however, the same spheres be now disturbed and mixed up, new points of contact will be attained, and the free space will be about the same as before deformation. Similarly, the deformed particles of wax had to be dispersed upon the microscope slide, and, when they rearranged themselves in a single plane upon the slide, they found new points of contact. As a result, while it could clearly be seen that the particles were facetted, the size of the pores between the packed particles upon the slide differed but little from the size of the pores between undeformed particles. In other words, it proved

impossible to demonstrate the essential point that, as the depth below the surface of the cake increases, the specific resistance increases, owing to the decrease of pore-size. Several attempts were made to induce the particles to shuffle into the required position, i.e., with facets in contact, e.g., by using liquids in which wax is partly soluble to disperse the particles, by tapping the slide, but eventually the attempt had to be abandoned.

A Criterion in the Use of Filter Aids.

It is common, in industrial practice, to assist the filtration of slurries which give slimy cakes by mixing a filter aid into the slurry. As this increases the total concentration fof solids in the slurry, we should expect, at first, that this would lead to a decrease in the rate of filtration. Normally, indeed, this would be the case, but the particles of a filter aid are comparatively coarse and rigid, and tend, therefore, to give the cake a more open structure. Shape, also, has an influence, so that the varieties of kieselguhr in which the particles are needle-shaped form the most general and most efficient of filter aids, for these needles interlock to give a very porous, rigid cake-skeleton.

It seems obvious that the proportion of filter aid to be used is a matter of importance, especially in the case of kieselguhr filter aids, for these are expensive materials. Yet, in most cases, the proportion of filter aid is decided

by a few rough experimental runs, the time-discharge curves of which are not even submitted to any analysis. There are not published, at the present time, any systematic experiments which indicate the relation between the capacity of a filter and the proportion of filter aid in the slurry.

The following discussion of experiments set forth in Table XIX. is intended as a help to filling this gap.

In these experiments, kieselguhr was added as a filter aid to slurries of ferric oxide. The resulting mixtures obeyed equation (24), just as do slurries of ferric oxide or of kieselguhr alone, i.e., θ/V' plotted against V' gives a straight line, $\theta/V' = bV' + a$

and we can calculate r_1 according to $r_1 = 2bPA^2/\eta c$

For any given mixture, r_1 is dependent upon P alone. The practical point to be noted from this is that r_1 is independent of the total concentration of ferric oxide and of kieselguhr, as long as the proportion of kieselguhr to ferric oxide remains unaltered. The proportion of filter aid to be added to a slurry should, therefore, always be expressed as a proportion of the solids in the slurry, not of the volume or of the weight of the slurry itself, as is usually the case.

Thus, in relating r_1 to the proportion of kieselguhr present, we should plot r_1 vs. percentage of kieselguhr, x, in the total solids in the cake, or vs. the ratio of kieselguhr to ferric oxide. Of the two, the former is

TABLE XIX. Experiments with Mixtures of Kieselguhr with Ferric Oxide.

Area of Filtering Surface = .342 Sq.dm.

Expt.	x percentage kieselguhr in mixture	c kgs. of ferric oxide per litre	η centi-poises	r_1 at 9.4 lb./sq.in. $\times 10^{-6}$	r_1 at 25. lb./sq.in. $\times 10^{-6}$	r_1 at 50. lb./sq.in. $\times 10^{-6}$	r_1 at 100. lb./sq.in. $\times 10^{-6}$	S
1.	0.0%	.004	1.05	7.15	8.45			
2.	"	.005	1.06	7.3	8.35	9.4		
3.	"	.010	1.08		8.25	9.25	10.7	
								.17
4.	4.7%	.0045	1.02	7.4	8.5	9.9		
5.	"	.009	1.06	7.15	8.45	9.9		
6.	"	.009	1.14		8.7	9.95	11.4	
7.	".	.009	1.14			10.0	11.4	
								.185
8.	16.1%	.0035	1.07	6.0	6.8			
9.	"	.007	1.06		6.8	7.45	8.85	
10.	"	.007	1.04			7.65	8.95	
								.14
11.	30.8%	.011	1.08	3.65	4.05	4.45		
12.	"	.010	1.08		4.2	4.4	5.35	
13.	"	.020	1.10			4.35	5.3	
								.11
14.	57.2%	.005	1.08	4.05	4.05	4.15		
15.	"	.005	.98		4.0	4.3		
16.	"	.009	1.06		4.0	4.2	4.8	
17.	"	.010	1.11			4.15	4.75	
								.03

the better plot, as it gives a closed range of abscissae, from x % = 0% for ferric oxide alone to x % = 100% for kieselguhr alone.

We have also a choice in methods for calculating r_1 depending upon how we evaluate the concentration, c. We can take c as the total concentration of solids in the slurry, or we can take it as the concentration of ferric oxide in the slurry. As it is the ferric oxide which we desire to remove, the latter method will give the truest comparison for different proportions of filter aid. Thus, if r_1 for a slurry of ferric oxide has twice the value of r_1, calculated on the concentration of ferric oxide, for a slurry of the same concentration of ferric oxide, with kieselguhr added, we are able to say at once that the latter slurry will filter at twice the rate of the former, for, in equation (24),

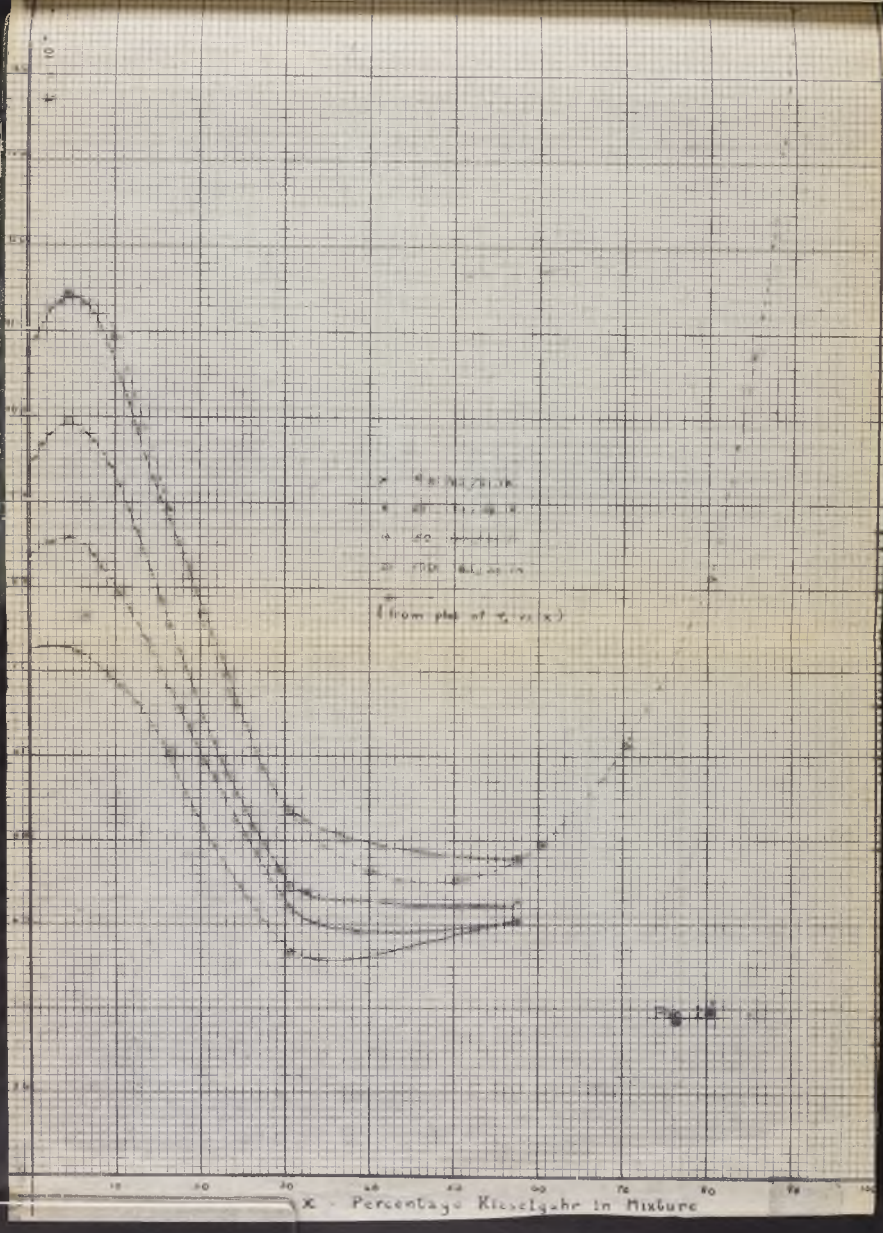
$$dV/d\theta = PA^2/\eta r_1 c(V+V_0).$$

P, A, η, and c are kept constant, i.e.,

$$dV/d\theta \propto 1/r_1(V+V_0).$$

Thus the values of r_1 in Table XIX. are calculated on the concentration of ferric oxide.

In Fig.24, these values of r_1 are plotted against x, the percentage by weight of kieselguhr in the cake solids. Each curve corresponds to a different pressure of filtration. According to these curves, r_1 increases at first, and then decreases to a minimum value, which is well below the initial value. The course of the curves was not


x - Percentage Kieselguhr in Mixture

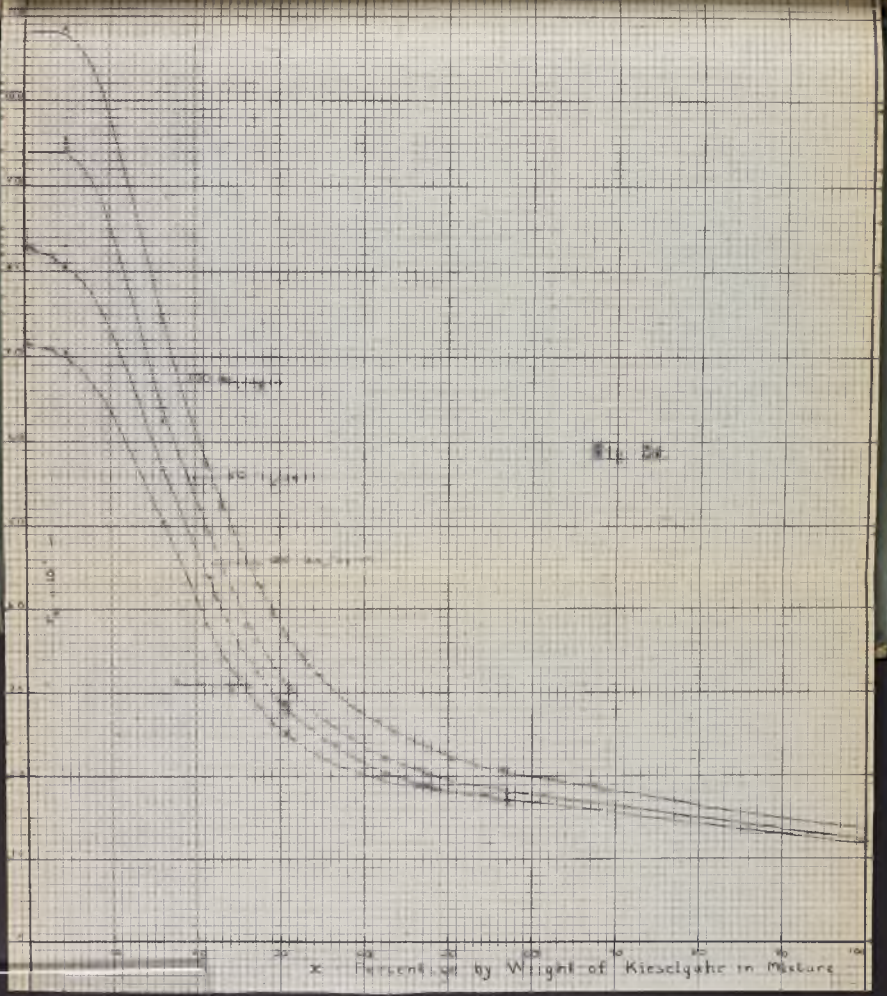
followed beyond x % = 57.2%, but they must, at some stage, rise to a value of $+\infty$ at $x=100$, since, for 100% kieselguhr, the concentration of ferric oxide is nil, i.e., in

$$r_1 = 2bPA^2/\eta c \quad , \quad c = 0.$$

The rise in r_1 for low percentages of kieselguhr is justifiable, for, if kieselguhr particles are scattered through the cake of ferric oxide without touching one another, they will increase the bulk, and hence the resistance of the cake without altering its texture to any appreciable extent.

It is evident that r_1 forms a criterion for filter aids. We cannot, indeed, label any substance a filter aid, but have rather to define that " a substance acts as a filter aid whenever the value of r_1 in the presence of the substance is lower than the value of r_1 in its absence."

The values of r_{1t} , the specific resistance calculated on th total concentration, have also a practical value. In Fig.25, these values have been calculated for kieselguhr-ferric oxide mixtures, and plotted against x . Now, in Fig.24, experimental values of r_1 represented the results of ~~four~~ seven teen experiments. Though this is a large number of experiments for a single series of mixtures, the points are too few in number. The curves are not definite in shape, and they stop short at $x=57.2$. On the other hand, there is little doubt as to the shape of the curves in Fig.25. To obtain accurate curves of r_1 vs. x with as little labour as possible, therefore, it is best to plot r_{1t} vs. x , and to


x Percentage by Weight of Kieselguhr in Mixture

calculate the points for r_1 vs. x from the resulting curves. If c be the concentration of ferric oxide in the slurry, so that $r_1 = 2bPA^2/\eta c$, then the total concentration of solids in the slurry, c_t, is given by $c_t = \frac{100}{(100-x)} \cdot c$, so that

$$r_{1t} = 2bPA^2/\eta c_t$$

and thus $r_1 = r_{1t} \cdot c_t / c = r_{1t} \cdot 100/(100-x)$.

This procedure has been followed for the 100 lb./sq.in. curve in Fig.25 to obtain the dotted curve in Fig.24. This dotted curve shows that the shape of the full-line curve through the experimental points is only approximately correct; and the dotted curve has the added merit of indicating clearly the point at which r_1 begins to increase to its final value of $+\infty$.

In Fig. 26, there are given the curves of r_1 vs. x for mixtures of ferric oxide with whiting. The results appear in Table XX. The curves form an interesting contrast to those in Fig.24. Whiting does not act as a filter aid at all. r_1 shows little change at first, and then increases steadily above its initial value to the final value $+\infty$. The relation between the curves in Fig.24 and in Fig.26 should be made clear by the following discussion.

When we add coarse particles to a slurry, there are two opposing effects on the resistance of the cake, (i) the increase in the volume of the cake tends to increase the resistance, (ii) the cake is given a more open texture, which

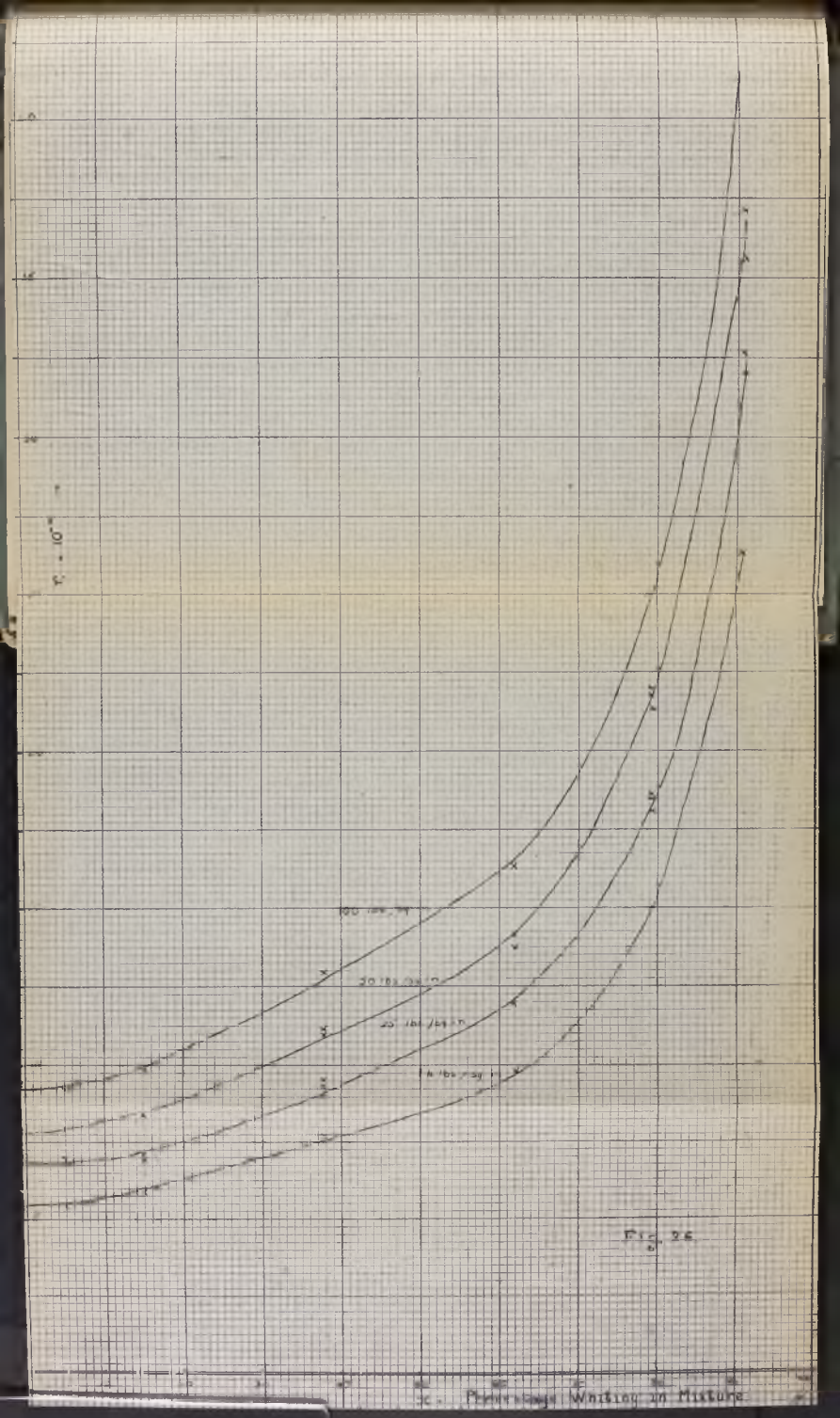


Fig. 26

% Phenol by Weight in Mixture

TABLE XX. Expariments with Mixyures of Whiting with Ferric Oxide.

Area of Filtering Surface .342 sq.dm.

Expt.	x percent. whiting in mixture	c kgs. of ferric oxide per litre.	η centi-poises	r_1 at 9.4 lb. sq.in. $\times 10^{-6}$	r_1 at 25. lb. sq.in. $\times 10^{-6}$	r_1 at 50. lb. sq.in. $\times 10^{-6}$	r_1 at 100. lb. sq.in. $\times 10^{-6}$	S
1.	0.0%	.005	1.10	5.45				
2.	"	.0071	.97	5.7	6.9			
3.	"	.0102	1.14		7.15	7.95	9.45	
								2.25
4.	5.75%	.0045	1.12	5.5				
5.	"	.009	1.11		7.0	8.0	9.3	
								2.25
6.	15.5%	.00375	.96	5.95	7.0			
7.	"	.0075	.97		7.15	8.45	9.95	
								2.25
8.	38.2%	.005	1.06	7.75	9.45	11.2		
9.	"	.005	1.07		9.55	11.0	13.0	
								2.2
10.	62.2%	.0025	.96	9.85	12.0	14.2		
11.	"	.005	1.06		12.0	13.8	16.4	
								2.2
12.	79.5%	.0025	1.10	15.0	18.7	22.0		
13.	"	.0025	1.06		18.2	21.8		
14.	"	.005	1.04		18.6	21.4	25.0	
								2.15
15.	91. %	.00197	1.06	26.4	32.0	37.1		
16.	"	.00415	1.06		32.7	35.6	41.2	
								1.8

tends to decrease the resistance. As already pointed out, when only a small proportion of coarse particles is added, they are dispersed through the cake and are not able to affect its texture very much, so that the "volume effect" is the more important, i.e., r_1 increases. This is well shown when kieselguhr is added to ferric oxide. When the percentage of coarse particles is increased, they are able to form little clumps in the cake, and, eventually, they form the main skeleton of the cake, in the voids of which are lodged the fine particles. If a slurry of kieselguhr be allowed to settle, we find it forms a bulky sediment, which it is very difficult to re-disperse by shaking. Evidently, its large, needle-shaped particles are very suited for interlocking to a rigid cake-skeleton of high porosity. Thus, when sufficient proportion of kieselguhr is mixed with ferric oxide, the structure of the cake is similar to that of a cake of kieselguhr, and the texture of the cake becomes sufficiently open to overbalance the effect of its increased bulk. It is believed by the writer that the action of filter aids is almost wholly due to their effect on the texture of the cake, and that adsorption and other surface effects play very little, if any, part.

In contrast to kieselguhr particles, whiting particles are very much smaller and more rounded. Thus, even when they form the main structure of the cake, they are unable to alter its texture sufficiently to overcome the increase in its volume.

In Figs. 27 & 28, the results in Tables XIX. & XX. are plotted as log. r_1 vs. log. P . The practical use of these plots is for constructing curves of r_1 vs. α at pressures intermediate between those given in Figs. 24 & 26.

They have also a theoretical interest. In Tables XIX & XX are given the gradients, S , of these plots. If we turn first to the values of S in Table XIX., it will be noticed that log. r_1 vs. log. P is not a straight line for 16.1%, 30.8% & 57.2% of kieselguhr, but curves up at the higher pressures. Now, this curvature is also to be observed in the log. r_1 vs. log. P plot for 100% kieselguhr, as shown in Fig.15, and indicates that kieselguhr is present in sufficient proportion in these mixtures to form a continuous or nearly continuous rigid skeleton of kieselguhr particles. It is further to be noted that the gradient, S , for pressures up to 50 lb./sq.in., begins to decrease markedly in the 16.1% mixture, though, for the 4.7% mixture, it has a value of .185, which is not very different from the value of .17 for 100% ferric oxide. This certainly suggests that, in the 4.7% mixture, the continuous skeleton of the cake consists of ferric oxide particles, so that the compressibility of the cake is approximately that of 100% ferric oxide.

Turning now to the values of S in Table XX., we note that S only begins to decrease for the 80% mixture, and then descends rapidly to the value of .14 for 100% whiting.

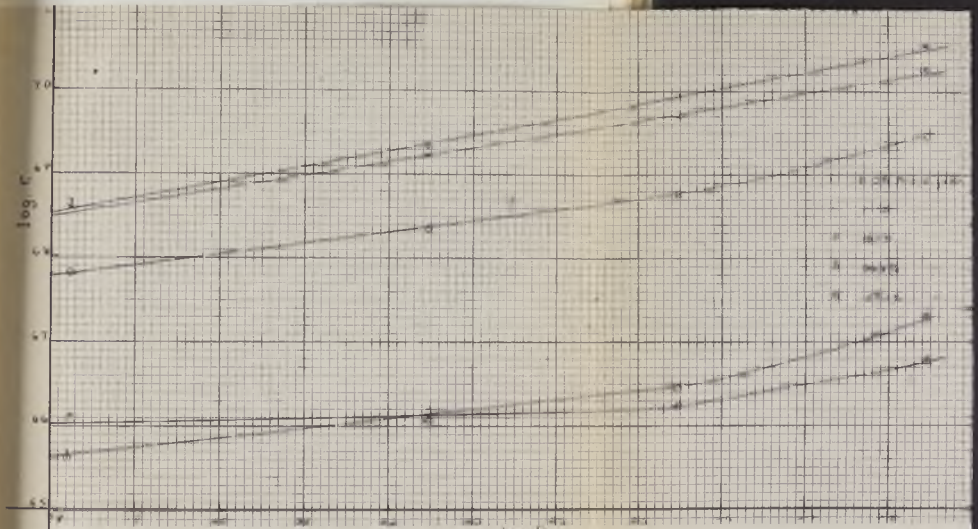


Fig. 27.

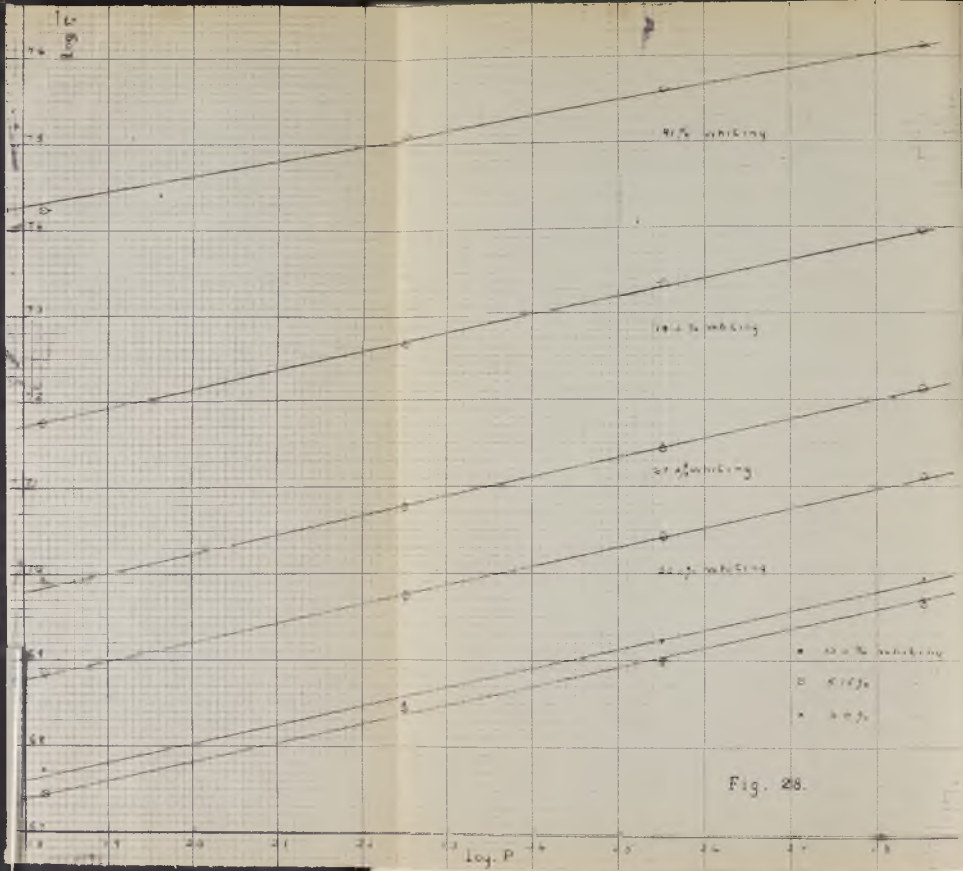


Fig. 28.

Ferric oxide must form the main skeleton of the cake up to nearly 80% of whiting.

In sharp contrast to this, S in kieselguhr mixtures shows a decrease for as little as 16% of kieselguhr. The difference must be due to the difference in size, shape and density of kieselguhr and of whiting particles. The specific gravity of whting is 2.81. That of kieselguhr is 2.24, but, as the particles are porous, the particle density must be much less, so that a given weight percentage of kieselguhr corresponds to a very much greater particle volume percentage than does the same weight percentage of whiting. Further, the comparatively large size of kieselguhr particles and their needle shape enables them to leave large voids when they pack together, so that a continuous skeleton of kieselguhr can have many more particles of ferric oxide packed into it than can the corresponding skeleton of whiting. As already discussed it is this packing effect, indeed, which enables kieselguhr to act as a filter aid.

A sedimentation analysis of ferric oxide and of whiting used in Table XX. was carried out in a Wiegner[17] sedimentation tube, and the size distribution curves are given in Fig.29. The particles of whiting prove to be mainly 5 - 10 times the size of the particles of ferric oxide. It can be shown that, for spheres of uniform diameter, arranged in the packing for minimum voids, small spheres of .2245 times their

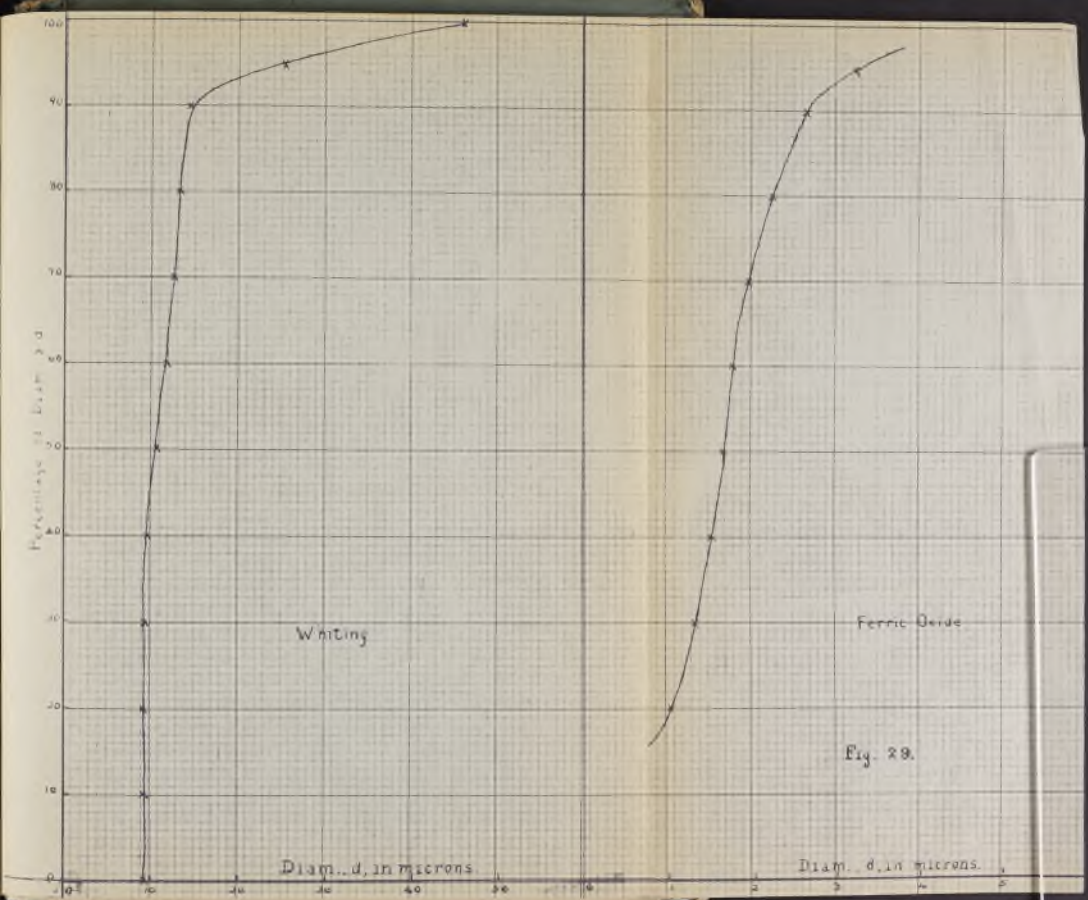

Percentage of Diam. > d
100
90
80
70
60
50
40
30
20
10
0
Whiting
Diam. d, in microns
10
20
30
40
50
Ferric Oxide
Diam. d, in microns
1
2
3
4
5

Fig. 28.

diameter, forming 3.28% of the total particle volume, can be packed into the voids without forcing the larger spheres apart. If the smaller spheres were smaller in diameter, say, .1 -.2 times the diameter of the larger spheres, and if they represented ferric oxide particles, while the larger spheres represented whiting particles, the value of S would be .14, the value for whiting, for the ferric oxide particles would be completely free from all deforming stresses in the cake. Somewhat more than 3.28% of such smaller particles could be packed into the voids, but it could be safely assumed that 5% would not be wholly accommodated, i.e., some of the ferric oxide particles would then force the larger particles apart to make room for themselves. Such particles then form part of the skeleton of the cake and are subject to the deforming stresses in the cake, so that the value of S should be intermediate between the value of .14 for whiting and .225 for ferric oxide. 80% by weight of whiting corresponds to 87.5% by volume, i.e., 12.5% by volume of ferric oxide particles, since the specific gravity of whiting is 2.81, and of ferric oxide is 5.12. The above reasoning shows that it is not unreasonable to assume that 12.5% by volume of ferric oxide particles is sufficient to separate all the whiting particles from one another. The continuous structure of the cake would then consist of particles of ferric oxide, and the value of S would be that for ferric oxide.

To summarise this section briefly, the curves of r_i vs. x are of the greatest practical importance for determining the efficiency of filter aids. These curves are plotted most accurately and completely by deriving them from the curves of r_{it} vs. x . The experiments for the curves are carried out at four or five standard pressures, and the curves for intermediate pressures can be derived from the plots of log. r_i vs. log. P .

These practical points have been illustrated by the experiments in Tables XIX. & XX., and Figs.24 - 28, derived from them. The same experiments have been utilised in an attempt to picture the behaviour of filter aids. The theoretical discussion is somewhat speculative, and is mainly intended as a suggestive interpretation of the experiments. The packing of particles of different shapes and sizes is a very complex and little-investigated field of knowledge, so that many more experiments than those here set forth are needed before it is possible to interpret with fewer simplifying assumptions.

SUMMARY.

If we take flow through a filter cake as analogous to that through a bundle of capillaries, it is possible to apply Poiseuille's Law to derive a filtration equation. Sperry first did this in 1916, though his equation contained some unnecessary terms, and omitted some necessary ones. Revised and completed, this equation becomes equation (24) of this thesis, namely, $dV/d\theta = PA^2/\eta r_1 c (V + V_0)$

wherein r_1 is called the specific resistance, and should be a constant. For ideal cakes, r_1 is constant, but, for compressible cakes, this is not true. By introducing the modification that r_1 is a function of the pressure of filtration, P, equation (24) is made to fit most of the results in the literature. Lewis and Underwood, respectively, have further modified the application of Poiseuille's Law, but it is shown that there is no necessity for such attempts, and the theoretical basis for these modifications is criticised.

The main part of the experimental work for this thesis is devoted to proving as rigidly as possible that equation (24) is perfectly general for all types of cake.

A new theory to justify that r_1 is a function of P for compressible cakes is described, according to which the specific resistance varies from cross-section to cross-section of the cake. It is contrasted with a theory advanced by Underwood, according to which the specific resistance is

constant throughout the cake ; and experimental evidence is given, which is interpreted as favouring the new theory.

The relation between r_1 and P does not prove to be very simple, but it can be expressed by $r_1 = r_1' P^s$ with sufficient accuracy for most practical purposes.

Certain limitations of equation (24) are described, when it is to be used for design, particularly in regard to sampling a slurry, and to segregation within the filter.

A final section applies the concept of "specific resistance" to determining the efficiency of filter aids.

BIBLIOGRAPHY.

1. Hatschek, J.Soc.Chem.Ind., 27, 538, 1908.

2. Almy and Lewis, J.Ind.Eng.Chem., 4, 528, 1912.

3. Sperry, Met.Chem.Eng., 15, 198, 1916.
ibid., 16, 161, 1917.
J.Ind.Eng.Chem., 13, 986 & 1163, 1921.
ibid., 18, 276, 1926.
ibid., 20, 892, 1928.

4. Hinchley, Ure and Clarke, Trans.Inst.Chem.Eng., 3, 24, 1925.

5. Walker, Lewis and McAdams, "Principles of Chemical Engineering", 2nd.Edn., p.365. (McGraw-Hill Book Co.)

6. Underwood, A.J.V., Trans.Inst.Chem.Eng., 4, 19, 1926.

7. Underwood, A.J.V., J.Soc.Chem.Ind., 47, 325T, 1928.
Proc.World Eng.Congr., Tokyo, (1929), 25, 76, 1931.

8. Gilse, Ginneken and Waterman, J.Soc.Chem.Ind., 49, 444T & 483T, 1930.
ibid., 50, 41T & 95T, 1931.

9. Ruth, Montillon and Montonna, J.Ind.Eng.Chem., 25, 76, 1933.
ibid., 25, 154, 1933.

10. Donald, unpublished communication.

11. Donald and Hunneman, Trans.Inst.Chem.Eng., 1, 97, 1923.

12. Weber and Hershey, J.Ind.Eng.Chem., 18, 341, 1926.

13. Phillips, Trans.Inst.Chem.Eng., 3, 25, 1925.

14. Young, Bull.Amer.Inst.Min.Eng., p.752, 1911.

15. Baker, J.Ind.Eng.Chem., 13, 610 & 1163, 1921.

16. Walker, Lewis and McAdams, (see Ref.5), p.370.

17. Wiegner, "Colloid Chemistry. Vol.I.", by Jerome Alexander, p.870, (1926), (Chemical Catalog Co.).

APPENDIX I.

If cake and cloth have different compressibilities, equation (24) cannot be derived as on p.23, and the following more general treatment must be used, in which the cloth and the cake are treated separately.

Suppose w_1 = weight of cloth per unit area = constant,

w_2 = weight of cake per unit area = cV/A

then $dV/d\theta = dp.A/\eta R_0 . dw_1$

$dV/d\theta = dp.A/\eta r . dw_2$

where R_0 and r are the specific resistances at any point in cloth and cake, respectively.

Case (i) Suppose we take $r = r' p^s$ and $R_0 = R_0' p^{s'}$ where s and s are both < 1, but have different values.

Then, for the cloth,

$$\eta w_1/A . dV/d\theta = \int_{P_2}^{P} dp/R_0 = \{P^{1-s'} - P_2^{1-s'}\}/(1-s') R_0'$$

i.e. $$\eta R_1/A . dV/d\theta = P\{1 - (P_2/P)^{1-s'}\}/(1-s')$$

where $R_1 = R_0' P^{s'} w_1$.

For the cake,

$$\eta w_2/A . dV/d\theta = \int_0^P dp/r = P_2^{1-s}/(1-s) r'$$

i.e. $$\eta r' P^s c V/A . dV/d\theta = P.(P_2/P)^{1-s}/(1-s).$$

Adding, for cake and for cloth,

$$\eta (r' P^s c V + A R_1)/PA^2 . dV/d\theta = (P_2/P)^{1-s}/(1-s) + \{1 - (P_2/P)^{1-s'}\}/(1-s')$$

Now, $P_2/P = (1 - P_1/P)$, so that, substituting, expanding, and discarding powers of P_1/P greater than two, we get

$$\eta (r' P^s c V + A R_1)/PA^2 . dV/d\theta = 1/1-s - P_1/P - s/2 (P_1/P)^2 + P_1/P + s'/2 (P_1/P)^2$$

i.e. $\eta(r'P^{s}cV + AR_1)/PA^2 . dV/d\theta = \{1 - \frac{1}{2}(s-s')(1-s).(P_1/P)^2\}/(1-s)$

$(s-s')$, $(1-s)$, $(P_1/P)^2$ are all less than unity, so that, if $P_1/P < \frac{1}{2}$ i.e., if $P_1/P_2 < 1$, it is perfectly safe to neglect $\frac{1}{2}(s-s')(1-s)(P_1/P)^2$ for all values of s and of s'. Indeed, if s and s are both $< \frac{1}{3}$, it is safe to say that $\frac{1}{2}(s-s')(1-s)(P_1/P)^2$ is negligible over the whole range of constant pressure filtration, i.e., from $P_1/P = 1$ to $P_1/P = 0$.

Hence $$dV/d\theta = PA^2/\eta(1-s)(r'P^{s}cV + AR_1)$$

or, putting $(1-s)r'P^{s} = r_1'P^{s} = r_1$

$$dV/d\theta = PA^2/\eta\{r_1cV + (1-s)AR_1\}$$

and, if $V_0 = AR_1(1-s)/r_1c$

$$dV/d\theta = PA^2/\eta r_1c(V+V_0).$$

This differs from equation (24) only in the condition that $P_1/P_2 < 1$ and that V_0 is not independent of P, since

$$V_0 \propto R_1/r_1 \propto P^{s'}/P^{s} \propto P^{s'-s}$$

Case (ii). Suppose $r = r''(1+\alpha p)^2$ and $R_0 = R_0''(1+\alpha' p)^2$ where α and α' are not equal.

Then, for the cloth,

$$\eta w_1/A . dV/d\theta = \int_{P_2}^{P} dp/R_0 = \{P/(1+\alpha'P) - P_2/(1+\alpha'P_2)\}/R_0''$$

i.e. $$\eta R_1/A . dV/d\theta = P\{1 - P_2/P . (1+\alpha'P)/(1+\alpha'P_2)\}$$

where $R_1 = R_0''(1+\alpha'P)w_1$,

For the cake,

$$\eta w_2/A . dV/d\theta = \int_0^{P_2} dp/r = P_2/(1+\alpha P_2) . 1/r''$$

i.e. $$\eta r_1cV/A^2 . dV/d\theta = P . P_2/P . (1+\alpha P)/(1+\alpha P_2)$$

where $r_1 = r''(1+\alpha P)$.

Adding, for cake and for cloth,

$$\eta(r_1 cV + AR_1)/PA^2 \cdot dV/d\theta = 1 - P_2/P \left\{ \frac{1+\alpha' P}{1+\alpha' P_2} - \frac{1+\alpha P}{1+\alpha P_2} \right\}$$

Since P_2/P, $\frac{1+\alpha' P}{1+\alpha' P_2}$, $\frac{1+\alpha P}{1+\alpha P_2}$, are all expressions nearly equal to unity during the greater part of a filtration, and since, when $\left(\frac{1+\alpha' P}{1+\alpha' P_2} - \frac{1+\alpha P}{1+\alpha' P_2} \right)$ is greatest, i.e., when P_2 is small, P_2/P is then at its least value, it is safe to say that the expression $P_2/P \left\{ \frac{1+\alpha' P}{1+\alpha' P_2} - \frac{1+\alpha P}{1+\alpha P_2} \right\}$ is negligible as long as $P_2/P_2 < 1$. A lower limit to P_1/P_2 might become necessary only if the compressibilities of cake and of cloth were very different, i.e., if α differed widely from α'.

Hence, $$dV/d\theta = PA^2/\eta(r_1 cV + AR_1)$$

and, if $V_0 = R_1 A/r_1 c$

$$dV/d\theta = PA^2/\eta r_1 c(V + V_0)$$

This differs from equation (24) only in the limit assigned to P_1/P_2 and in that V_0 is not independent of

i.e., $$V_0 \propto R_1/r_1 \propto 1 + \alpha' P/1 + \alpha P.$$